AN INTRODUCTORY COURSE IN

QUANTITATIVE CHEMICAL ANALYSIS

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CHEMICAL ANALYSIS

WITH

EXPLANATORY NOTES, STOICHIOMETRICAL
PROBLEMS AND QUESTIONS

BY

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PREFACE

THIS introductory course in Quantitative Analysis is designed for use with classes consisting of students who have completed courses in Elementary Chemistry and Qualitative Analysis, and who are beginning work in Quantitative Analysis. On the laboratory side, its primary intent is to provide the student with directions sufficiently detailed to offer little opportunity for going astray, and thus to enable him to work successfully without an undue amount of personal supervision. The instructor is thereby placed in a position, in the laboratory as well as in the classroom, to exert his personal influence more especially towards the development of theoretical knowledge and independent thought on the part of the students.

The use of the book in the laboratory should of course be supplemented by regular classroom instruction; and, with this in mind, it has seemed desirable to include the stoichiometrical problems of Part IV, and the questions of Part V. The problems of Part IV are such as are constantly met with in analytical work, and their conscientious study will give the student an insight into the principles of a wide variety of processes; the answers to the problems have been intentionally omitted. It is the writer's practice to require, as a written exercise to be handed in at the beginning of a recitation, the solution of a definite number of problems each week throughout the course; these are graded, and are returned at the end of the following recitation. The questions of Part V are for the most part answered in the notes or elsewhere in the book; but it has been the writer's experience that the beginner reacts more favorably to concrete questions assigned in advance for study, than to the same questions when put to him for the first time just after he is supposed

to have mastered the principles and details of a specific analytical process.

The general directions and discussions of Part I are intended to emphasize those matters, both of theory and practice, which should receive especial attention from the worker in analytical chemistry. It is of course realized that a mere reading of Part I will not go far towards familiarizing the student with its contents; but it is sought to accomplish this end by referring later on in the text to special subjects as occasion presents.

The analyses selected for practice, included in Parts II and III, are those which are comprised in the elementary courses of quantitative analysis at the University of Illinois. They have been chosen as being satisfactory types of gravimetric and volumetric analysis, and, after several years' experience, they are considered to afford to all classes of students a suitable foundation for more advanced work. It is believed that they furnish also a good insight into the methods of quantitative analysis, and hence are adapted to the needs of students who will not extend their study beyond the period of an introductory course.

In addition to the help derived from other books and from journal articles, the writer wishes to acknowledge his especial indebtedness in the preparation of this manual to the following works on analytical chemistry: H. P. Talbot's *Quantitative Chemical Analysis;* J. W. Mellor's *Treatise on Quantitative Inorganic Analysis;* W. F. Hillebrand's *The Analysis of Silicate and Carbonate Rocks;* F. P. Treadwell's *Lehrbuch der analytischen Chemie;* W. C. Blasdale's *Principles of Quantitative Analysis;* and A. Fischer's *Elektroanalytische Schnellmethoden.*

<div align="right">G. McP. Smith.</div>

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CONTENTS

PART I

vii

PART II

GRAVIMETRIC ANALYSIS

PART III

VOLUMETRIC ANALYSIS

PART IV

STOICHIOMETRY

PART V

APPENDIX

AN INTRODUCTORY COURSE IN

QUANTITATIVE CHEMICAL ANALYSIS

PART I

INTRODUCTION

A. GRAVIMETRIC AND VOLUMETRIC ANALYSIS

QUANTITATIVE analysis has for its object the determination of the quantities of the elements or compounds which are present in particular samples of material. The results are usually expressed in terms of percentage, ordinarily by weight; but sometimes, as in the analysis of gases, by volume.

The procedure to be employed in a specific case will often depend upon the qualitative composition of the sample. A qualitative analysis, therefore, should always precede a quantitative, unless the composition of the sample is sufficiently well known.

In the performance of quantitative determinations there are two principal methods of procedure, according to which the subject is subdivided into *gravimetric* and *volumetric* analysis. In addition, there are gasometric methods, and various physical methods, of analysis; but these will not be described in this book.

In a *gravimetric analysis*, a weighed sample is taken, and the substances to be determined are separated, one after another, either in the free state, or in the form of suitable compounds. Each final product is weighed, and, from its weight, the weight, and therefore the percentage, of the corresponding substance in the sample can be calculated.

The substance to be weighed is in most cases separated from solution by precipitation, though in many instances it is deposited upon a weighed cathode or anode by electrolysis. Sometimes it is separated from other substances by extraction with a solvent, and sometimes in the form of a gas, the weight of the gas being determined either by absorbing it in a weighed quantity of some substance and noting the increase, or by noting the decrease in weight due to the removal of the gas alone.

In a *volumetric analysis* a weighed sample is also taken, but the quantity of the substance to be determined is arrived at by causing some well-defined reaction to take place, the reagent being added from a burette, in the form of a solution of known concentration. This operation is called *titration*. From the volume of the solution added, it is easy to calculate the weight of the substance present in the sample.

In many instances, it is necessary in volumetric analysis also to separate the substance to be determined from interfering substances present with it in the sample; but, instead of making a final weighing, the substance is again brought into solution, in suitable form, and its quantity estimated by titration.

In order to illustrate the two methods, let us consider the determination of chlorine in sodium chloride.

(*a*) **Gravimetric Method.** The weighed sample is dissolved in water, the solution acidified with nitric acid, and the chlorine converted into insoluble silver chloride by means of an excess of silver nitrate solution. The precipitate is filtered off, washed, dried, and weighed. From its weight, the weight of chlorine may be calculated, as follows:

$$\frac{Cl}{AgCl} \times \text{wt. of precipitate} = \text{wt. of chlorine.}$$

And, of course, $\dfrac{\text{wt. of chlorine}}{\text{wt. of sample}} \times 100 = \%$ of chlorine.

(*b*) **Volumetric Method.** The weighed sample is dissolved in water, the solution acidified with nitric acid, and the chlorine converted into silver chloride by the gradual addition, from a burette, of a silver nitrate solution of known concentration. As soon as, after stirring each time and allowing the precipitate to settle, the first drop is added which fails to produce a precipitate, the reaction is known to be complete; and the number of cubic centimeters required, multiplied by the chlorine equivalent of the silver nitrate contained in each cubic centimeter, gives directly the weight of chlorine in the sample.

B. GENERAL REMARKS CONCERNING QUANTITATIVE WORK

Neatness. The drawers and cupboards of the desk, and all apparatus, should at all times be neat and clean. A sponge or an old towel should always be at hand, and the desk top and filter-stands should be kept dry and clean. Vessels should be scrupulously clean, inside and out, and the outer surfaces of beakers, flasks, etc. should be wiped dry with a clean, lintless towel, before use.

If the inner surfaces of funnels, flasks, etc. become contaminated with a film of grease, they should be rinsed either with a strong solution of sodium hydroxide or with sulphuric acid-dichromate cleaning solution. (The latter may be prepared by pouring, cautiously and with stirring, 4 volumes of concentrated sulphuric acid (sp. gr., 1.84) into 3 volumes of cold water, and saturating the resulting hot solution, without further heating, with powdered sodium or potassium dichromate.) In extreme cases it may be necessary to allow the apparatus to stand overnight in contact with this solution.

Accuracy and Integrity. It is of fundamental importance in quantitative work to guard against loss of material or the introduction of foreign matter. All filters and solutions should be kept covered to protect them from dust, and in dissolving substances for analysis, the vessels should always be kept covered to prevent mechanical losses.

Success in quantitative work demands first of all a certain amount of dexterity in the performance of the mechanical operations involved. Certain individuals are able to acquire this skill with comparative ease, but the majority of persons can acquire it only through patient and persistent application. If the student finds himself unable to do as good work as his more experienced or more fortunate neighbor, he should rather devote his energies to increasing his proficiency than to trying to conceal his lack of it. Nothing less than absolute integrity can be

demanded of an analytical chemist, and any disregard of this principle is certain to be fatal to his success.

Economy of Time. An economical use of laboratory hours is best secured by acquiring a thorough knowledge of the character of the work to be done before undertaking it, and then arranging the work so that no time shall be wasted during the evaporation of liquids and other time-consuming operations.

At least two determinations should be in progress at the same time, and confusion should be carefully guarded against by a free use of labels. In general, economy of time results from the evaporation or filtration of several solutions at once; four or more precipitates may often be washed in the time required for any one of them, if taken alone.

Notebooks. Notebooks should contain, besides the analytical data, descriptive notes regarding any special difficulties encountered in the analysis and the remedies applied, and also any incidents in the course of the analysis which might influence the results injuriously.

All analytical data, such as records of weights and volumes, should be placed upon the right-hand page, while the left-hand page should be reserved for the descriptive notes, the calculation of factors, of the amounts of reagents required, etc.

All analyses should be made in duplicate, and in general a close agreement in results should be expected. It should, however, be realized that " check results " do not furnish conclusive evidence of accuracy. Since check results depend almost entirely upon the prevalence of identical conditions throughout the course of the two analyses, they are apt to be obtained even when inaccurate methods of analysis are employed. *A common fallacy is to the effect that no part of the work need be performed more carefully than that part which is necessarily least accurate.* For example, it is said that if a certain step in a process involves an unavoidable error of 0.1%, it is a waste of time to attempt to avoid errors in other parts of the work amounting to 0.05% or even 0.09%. This unfortunate attitude would lead to the

conclusion that if a method cannot yield results involving an error of less than 0.10%, it should be given a chance to depart 0.10% + $n \times 0.09\%$, if there are n other places where errors may occur. Of course these errors *may*, to a certain extent, counteract one another in effect, but there is no assurance that they *will* do so. Nevertheless, when a certain minimum error is unavoidable, *e.g.* 0.20%, it is not wise to expend an undue amount of time in trying to prevent other possible errors when the ratio of these errors to the larger error is very small; because in such a method the percentage result has no significance whatever beyond the first decimal. It is a good rule always to *report one decimal place further than the one that is considered to be certainly correct.*

All records should be dated, and all observations should be recorded at once in the notebook. Records should never be made upon loose sheets of paper. Since the neat and systematic arrangement of the analytical data in the notebook is a matter of the first importance, the following sample right-hand page is given as a suggestion of the manner in which such records should be kept. In the analysis here given, it is uncertain whether the first figure after the decimal should be 4, 3, or 2; of course, then, nothing is known concerning the value of the second figure, which therefore is not included in the mean result.

DETERMINATION OF CHLORINE IN A SOLUBLE CHLORIDE — SEPT. 21–28

	I	II
Sample Tube, etc.	8.4237	8.2377
Tube minus Sample	8.2377	8.0198
Wt. of Sample	0.1860	0.2179
Wt. of Crucible	5.3588	5.0072
Crucible+AgCl, 1st time	5.7830	5.5024
2d time	5.7828	5.5023
Wt. of Crucible	5.3588	5.0072
Wt. of AgCl	0.4240	0.4951
Per cent of Chlorine	56.40	56.21

Mean Value = 56.3%

Reagents. Probably the greatest hindrance to good work in otherwise well-equipped laboratories is the difficulty of securing satisfactory reagents. Also much of the glassware on the market is of an inferior grade and utterly unsuited for analytical work.

The habit of carefully testing reagents, including distilled water, cannot be too early acquired; the most ceaseless vigilance should at all times be practiced in guarding against the presence of impurities which would vitiate the analytical work under way. As is generally known, a " C. P." label is no guaranty whatever of the purity of a reagent, and the " guaranteed " or " analyzed " reagents, sold at high prices, are at times worse than products for which no claim to special purity has been made.

Acids of a high degree of purity can be obtained commercially, and, although exceptions have been noted, these in most cases need no redistillation. But, owing to its basic nature, ammonia ought always to be redistilled at short intervals, after first shaking it up with slacked lime to remove any carbonic acid. Glass stock bottles may be coated inside with ceresin, to prevent contact between the glass and the ammoniacal solution.

Owing to the solvent action on glass of many solutions of solid reagents, these should be made up at frequent intervals in limited quantities, or, preferably, the solid should be dissolved as wanted. This is particularly called for with such reagents as ammonium oxalate and microcosmic salt, and alkaline " magnesia mixture " should not be kept in contact with glass.

The stopper of a reagent bottle should never be laid upon the desk, but should always be held in the fingers until returned to the bottle. This will prevent contamination, whether due to an interchange of stoppers, or to some other cause. The necks and mouths of such bottles should of course be kept scrupulously clean.

C. THE OPERATIONS OF ANALYTICAL CHEMISTRY

The chief operations involved in analytical work which can be profitably discussed at this point are weighing, precipitation, filtration, and the washing of precipitates, the drying and ignition of precipitates, the evaporation of liquids, and the volumetric measurement of liquids.

These operations will be described in the following sections, which should be studied carefully by the beginner. It is of prime importance for success as an analyst to pay great attention to details and scrupulously to avoid any conditions which may destroy the analysis, or lessen confidence in the accuracy of the data.

The adoption of the suggestions given will do much to insure work of a high grade, while neglect of them will often lead to inaccurate results and loss of time.

I. WEIGHING

The purpose of weighing is to compare the quantity of matter in a specific object with the quantity of matter in a given standard — a gram or kilogram weight. The comparison is made on the balance by suspending the object to be weighed at one end of a beam, and the weights at the opposite end of the beam. The beam is virtually a kind of lever, and the mechanical theory of the balance is founded mainly on the properties of levers.

The Balance. The beam of the balance is supported on a central knife-edge, usually of agate, which rests upon a plane agate plate; and two pans for supporting the masses to be compared are vertically suspended from stirrups, each of which has an agate bearing which rests on a knife-edge fixed at one extremity of the beam. The arms of the balance are so graduated that a rider (of known weight) can be placed on the beam at any required distance from the central knife-edge.

If the three knife-edges are allowed to press continually upon their agate bearings, they soon become blunted, and wear fur-

rows in the bearings.   In order to prolong the life of the knife-edges and bearings, the balance is provided with a " release " which separates the knife-edges from their bearings when the balance is not in use.   If the balance shows signs of stiffness in the motion of beam and pans, the fault should be investigated at once.   The defect may be due to an accumulation of dust between the knife-edges and their bearings; to the blunting of the knife-edges; or to the wearing of furrows in the bearings. To prevent the accumulation of dust, and also to prevent the interference of air currents while weighing, the balance is inclosed in a glass case.

In order to render small movements of the beam perceptible, there extends downwards from its center a long pointer which multiplies the rotational displacement.   When equilibrium is established, the lower end of the pointer should come to rest in front of the zero of a scale which is located immediately behind this end.

The conditions which must be satisfied by a good balance are : (1) The balance must be consistent.   It must give the same result in successive weighings of the same body.   This condition depends upon the trueness of the knife-edges.   (2) The balance must be accurate.   At rest the beam must be horizontal when the pans are empty, and when equal weights are placed upon the pans.   This condition depends upon the equality of the two arms.   (3) The balance must be stable.   The beam after being displaced from its horizontal position must return to its horizontal position.   This condition depends upon the adjustment of the center of gravity.   (4) The balance must be sensitive.   It must show even a very small inequality in the two masses on the scale pans.   This condition depends largely upon the length of the arms.   (5) The balance must oscillate with reasonable rapidity.   Short beams oscillate more rapidly than long ones.

The analytical balance will perform excellent service under the proper conditions, but great care in its use is essential if its

accuracy is to be relied upon. It should be located in a room that is free from dust and fumes, and should stand upon a support that is free from shocks and vibrations.

The Use and Care of the Analytical Balance. The following rules embody the main points to be observed in the use and care of a balance.

(1) Each student must feel a personal responsibility for the proper use of his balance; carelessness on the part of any one is apt to render inaccurate not only his own work, but also that of all others who use the same balance.

(2) The balance pans should be brushed off, if necessary, and the adjustment of the balance tested before use.

The balance is properly adjusted only if the following conditions are fulfilled: (*a*) The spirit level or plumb bob inside the balance case should show that the balance is level; (*b*) the mechanism for raising and lowering the beam should work smoothly; (*c*) the pan arrests should just touch the pans when the beam is lowered; (*d*) the pointer should rest at zero when the beam is raised, and also when it is lowered so that the pan arrests touch the pans; and (*e*) the pointer should swing equal distances on either side of the zero-point when the beam is set in motion without any load on the pans. In the latter case, if the variation does not exceed two divisions on the scale, it is hardly worth while to disturb the balance by an attempt at correction; it is better to make a proper allowance for the small zero error.

(3) The beginner should never attempt to make adjustments himself, but should always apply to the instructor in charge.

(4) The beam should never be set in motion by lowering it upon its knife-edge, nor by touching the pans, but rather by means of the rider; however, there is a " trick " in lowering the *pan supports* so that the oscillations of the pointer will have the required amplitude.

The pans should be arrested and the beam raised before any change is made in the load or weights on the pans except in the case of the small fractional weights, when it is only necessary

to arrest the pans. The object to be weighed and the heavy weights should be placed in the middle of their respective pans, since a heavy load near the edge of a pan is apt to cause troublesome oscillations.

The beam and stirrups should never be left upon their knife-edges, and the motion of the beam should be arrested only by means of the pan arrests, and only when the pointer is passing the center of the scale; otherwise the knife-edges become dull and their agate bearings furrowed.

(5) The weights should be cared for not less than the balance, and should be standardized by the analyst unless they are known to be in satisfactory condition.

The weights should be handled carefully, and only with the forceps provided for that purpose; they should never be touched with the fingers. In weighing, the weights should always be placed upon the same pan, and they should be taken in the order in which they occur in the box, the larger ones first; and the weight of the object should be recorded by noting the vacant spaces in the box. The record so obtained should be checked as the weights are removed from the pan. In this way errors are not likely to occur.

(6) No analytical sample should ever be placed directly upon the balance pan. Furthermore, the object to be weighed should neither be warmer nor colder than the air in the balance case. Currents of hot air may impinge on the arms of the balance and buoy up the beam, or cause one arm of the balance to expand unequally.[1] If the object is colder than the atmosphere of the balance case, moisture may condense on its surface. If the body to be weighed is likely to be electrified (*e.g.* a glass weighing tube), it should be allowed to stand for some time after it has been wiped, before weighing.

(7) The balance case should be closed while weighing with the rider, so as to avoid currents of air.

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[1] For instance, a platinum crucible which appeared to weigh 20.649 g. when warm, weighed 20.6920 g. when cold.

As soon as the object is apparently balanced by the weights, the beam should be raised and again lowered into place, and the observation repeated. This will assure the proper alignment of the beam and pans at the time when this is most important.

(8) In using weighing bottles or tubes, the vessel should be weighed together with its contents. A quantity suitable for analysis should then be removed without loss, and the vessel and contents again weighed. The difference in weight indicates the quantity of sample taken.

Cork stoppers in weighing tubes are apt to change in weight, owing to varying amounts of moisture absorbed from the atmosphere. It is therefore necessary, before weighing out a new sample from it, to confirm the recorded weight of a tube which has been unused for some time.

(9) *Errors in weighing should fall well within the limits of the experimental error due to the analytical operations.* If, for example, an error of 0.001 g. were made in weighing out a gram sample of clay containing 0.20% of MgO, the resulting error in the determination of the magnesia could be no greater than 0.1% of its value; the final result could not be affected by more than 0.1% of 0.20%, *i.e.* 0.0002%. This is negligibly small. Suppose, however, that an even smaller error of 0.0005 g. were made in weighing the 0.0055 g. of $Mg_2P_2O_7$; this would represent an error of 9% of the magnesia value, which is inexcusable.

(10) If any substance is spilled upon the pans, or if anything at all appears to be the matter with a balance, the fact should at once be reported to the instructor in charge. In most instances serious injury can be averted by prompt action.

Determination of the Zero-point. Lower the beam and stirrups upon the knife-edges by slowly turning to the left the milled head at the front of the balance case. Then release the pan supports by gently pressing inwards the small button, also at the front of the case, and with the beam swinging smoothly, make a consecutive record of the number of scale divisions traversed by the pointer on either side of the center. Record

the swings to the left as negative numbers and those to the right as positive numbers, making four observations on one side and three on the other.   Take the average of each column, add these averages algebraically, and divide the sum by two.   The quotient is the zero-point of the balance, *i.e.* the position on the scale at which the pointer would finally come to rest.

Example :

LEFT		RIGHT		
	−6.8		+4.7	
	−6.6		+4.5	
	−6.4		+4.3	
	−6.3			
Average :	−6.5	Average :	+4.5	Zero-point = −1.0.

Two methods of procedure are now open to the operator. He may either make his weighings with reference to this observed zero-point or he may adjust the balance so that the observed zero-point is the actual zero of the scale.   The first method is preferable, unless the zero-point is more in error than one scale division.   The zero-point is apt to change, and it must be determined each day, or even more often.

Methods of Weighing.   Weighings smaller than 0.005 g. (or 0.01 g.) are made with the rider.   When the arms are divided into five divisions, a 5-milligram rider is used ; in general, the rider should weigh as many milligrams as there are large divisions on the beam between the central knife-edge and the right-hand stirrup support.   Each division on the beam then corresponds to a milligram.

Ordinary Method.   The object to be weighed is placed upon the left-hand pan of the balance and weights upon the right-hand pan, until, finally, the further addition of 5 mg. (or 10 mg.)more than counterbalances the object.   This weight is then removed, the balance case closed, and the rider adjusted so that the pointer swings equal distances on either side of the zero-point.   This

method of weighing is very common, and it is sufficiently accurate for ordinary analytical work. If necessary, the zero-point of the unloaded balance should be determined before each weighing.

In special cases, as in the calibration of a set of weights, it is important to make more accurate weighings. It is here best to use the method of weighing by double vibrations, which from the following description may appear somewhat laborious; but the labor is more apparent than real.

Method of Weighing by Double Vibrations. (*a*) Find the zero-position of the pointer in the case of the unloaded balance, according to the method already described. Let us suppose this to be at +0.1.

(*b*) Find the deviation of the scale per milligram, that is, the sensitivity of the loaded balance. The object to be weighed is placed upon the left pan, the weights on the right pan. When the weights are so far adjusted that an additional 0.005 g. (or 0.01 g.) would be too much (*e.g.* weight on pan = 11.216 g.), close the door of the balance case, and adjust the rider until the pointer swings on both sides of the zero of the scale. Now find the position of rest, which we will suppose to be at +0.8. Move the rider one milligram division to the right, and again find the position of rest; this being at, say, −2.1. Hence, the zero-point is displaced +0.8 − (−2.1) = 2.9 divisions by increasing the weight 1 milligram; or 2.9 scale divisions correspond to 1 milligram for the given load.

(*c*) Calculate the weight of the load on the pan. From the preceding results, it follows that the load weighs 11.216 + *x*. The zero-point of this load is displaced 0.8 − 0.1 = 0.7 scale division. Since 2.9 scale divisions correspond to 1 milligram, 0.7 scale division will correspond to $\frac{0.7}{2.9} = 0.24$ mg. Hence the weight of the body is 11.216 + 0.00024 = 11.21624 g. These calculations may be summarized in the formula

$$\text{Correction} = +\frac{a-z}{a-b}\text{ mg.,}$$

in which z represents the zero-point of the unloaded balance; a, the zero-point with not quite enough weight on the right pan; and b, the zero-point with a milligram more on the right pan than corresponds to a.

Analytical balances will rarely indicate with certainty less than 0.0001 g. Hence, although the weight may be calculated as above to the fifth decimal, it should generally be rounded off by dropping the fifth decimal and raising the fourth decimal one unit when the dropped figure exceeds 5.

In certain cases, as in the calibration of volumetric measuring apparatus, it is necessary for the weight found to be independent of any inequality in length in the beam arms. In such cases, and in the determination of absolute weights (reduction to weights *in vacuo*), one of the following methods should be used.

Method of Gauss. Weigh the object first in one pan, then in the other. Let W be the true weight, a the weights required to counterbalance the object when it is on the left pan, and b the weights required when the object is on the right pan. According to the principle of moments:

$$Wl = ar; \text{ and } bl = Wr.$$

That is, $$W^2lr = ablr, \text{ or } W^2 = ab;$$
whence $$W = \sqrt{ab}.$$

Therefore the true weight is the square root of the product of the two observed weights.

Borda's Method of Weighing by Tares. Here the object, placed on the right-hand pan, is balanced by a suitable tare (weights, wire, beaker containing shot, etc.) on the left-hand pan. The object is then removed, and weights are added in its place until equilibrium is restored. These weights are necessarily the same in value as the object for which they substitute, irrespective of differences in the arms.

The Calibration of a Set of Weights. Fairly accurate weights can be purchased for a reasonable sum, and for most analytical work the inaccuracies of the better class of weights are negligibly

small in comparison with the errors of experiment, and the imperfections in the analytical processes.

An analyst, however, should *know* that his weights are sufficiently accurate, and for this reason he should calibrate the weights. The errors due to imperfections in the weights can easily be reduced to 0.0001 g. The weights should be tested at periodic intervals, say once or twice a year, depending upon the frequency with which they are used.

In special cases, *e.g.* in the calibration of volumetric apparatus, absolute weights may be required, but for general analytical work absolute weights are not necessary. If the weights are consistent with one another, their absolute values have no influence upon the accuracy of an analysis.

Before beginning the calibration, distinguish all separate pieces of the same denomination by marking them with a small prick punch. One of the two 10-gram pieces may be marked ('), two of the 1-gram pieces (') and (''), etc.

The method of weighing to be followed in the calibration will depend upon the degree of equality in the lengths of the beam arms. If they are unequal, either the method of Gauss or that of Borda may be used for comparing the weights. If the method of Borda is used, a second set of weights will be found convenient for the substitutions. This method involves less work in calculating then does that of Gauss. If the beam arms are essentially equal, the simple method of double vibrations is used, without the necessity of a correction. In any case, the following comparisons are made, with the use of the rider to obtain equilibrium.

I

Gram Weights

1 against 1'
1 against 1''
2 against 1+1'
5 against 2+1+1'+1''

10 against 5+2+1+1′+1″
10 against 10′
20 against 10+10′
Etc.

II

Fractional Weights

500 against 200+100+100′+50+20+10+10′+5+rider at 5
200 against 100+100′
100 against 100′·
100 against 50+20+10+10′+5+rider at 5
50 against 20+10+10′+5+rider at 5
20 against 10+10′
10 against 10′.
10 against 5+rider at 5
5 against rider at 5

Also unmarked 1-gram piece against all of the fractional pieces+rider at 5

The calculation of the weight of each piece of 1 gram and upward is made upon the arbitrary assumption that the unmarked 1-gram weight is correct. In calculating the weights of the fractional pieces, we first assume the unmarked 10-mg. piece as a standard and calculate provisional weights for each of the other fractional pieces upon this basis. We then add these provisionally corrected weights and determine by comparing the results with their collective weight as found in terms of the standard 1-gram piece, how much each weight must be further corrected. If, for example, the sum of the provisional fractional weights were found to be 5 (rider)+5+10+10+19.9 +49.7+100+100.1+200.1+499.2=999.0 mg., or 0.9990 g., while their collective weight in terms of the 1-gram standard = 1.0017 g., then each of the provisional values should be multiplied by $\frac{1.0017}{0.9990} = 1.0027$. In this way, we obtain the weight of each piece in the set in terms of the unmarked 1-gram weight.

If desired, we can then find the exact value of the unmarked 1-gram piece in terms of an absolute standard weight. For example, if the unmarked 1-gram weight is found by comparison

to weigh 0.9998 g., we have simply to multiply each weight in the table, based upon the unmarked 1-gram weight as a standard, by 0.9998, in order to obtain the weight of each separate piece of the set in terms of the absolute standard.

Errors Due to Inequalities in Length in the Beam Arms. In the preceding discussion, it has mainly been assumed that the two arms of the beam are equal in length. This is not really the case. It is mechanically impossible to insure perfect equality. To find the relative lengths of the arms, place (corrected) weights of the same nominal value — say, 50 grams — upon each pan, and bring the balance into equilibrium by means of the rider. Interchange the weights on the two pans, and again bring the balance into equilibrium by means of the rider. Call the two weights W and w, and let l and r respectively denote the additional weights required for equilibrium on the left and right sides. Then, on the first weighing, $w+l=W$; and, on the second weighing, $W=w+r$. Let L and R respectively denote the length of the left and right arm. Then from the law of levers,

$$L(w+l) = RW ; \text{ and } LW = R(w+r)$$

Solving each of these equations for W, and equating the results, we find that

$$\frac{L}{R}(w+l) = \frac{R}{L}(w+r)$$

whence,

$$\frac{L}{R} = \sqrt{\frac{w+r}{w+l}}$$

Suppose, for example, that the weighings were found to be:

LEFT	RIGHT
50	$= 20+10+10'+10''+0.13$ mg.
$20+10+10'+10'' = 50+0.19$ mg.	

Here, then, $l = -0.00013$, $r = +0.00019$, and $w = 50$ g. Consequently if in the above expression we let $R=1$, we have

$$L = \sqrt{\frac{w+r}{w+l}} = 1.0000032$$

i.e. $L : R = 1.0000032 : 1$

c

With this ratio, $\frac{L}{R} = 1.0000032$, a weight w on the left pan of the balance will be equivalent to a weight $w \times 1.0000032$ on the right pan. Hence, if a substance on the left pan balances the weight 50 g. on the right pan, the weight of the substance is $50.0000 \times 1.0000032 = 50.0016$ g. — an error of only 0.003 per cent. There is therefore no need to apply the correction. Each balance has its own constant $L : R$ for a given load; the numerical value of the ratio varies with the different loads.

Most analytical balances do not require a correction on account of inequalities in the arms; the arms are usually made sufficiently exact. Furthermore, if the weights are always placed, say, on the right pan, such a correction is unnecessary in ordinary analytical work, because, although there may be differences between the apparent and true weights of the substances weighed, these differences are proportional to the true weights and therefore do not affect the ratios obtained.

Errors Due to the Buoyancy of the Atmosphere. The assumption is made that, if two bodies are equal in weight at the same time and place, they contain the same mass or quantity of matter. This is only true if the two bodies have the same volume, or if the weighing is carried out in a vacuum. A body weighed in air is buoyed up by a pressure equivalent to the weight of the air which it displaces. Suppose that exactly 100 grams of platinum (sp. gr. 21.55) are weighed in air with brass weights (sp. gr. 8.4). Then 4.5 cc. of air, at say 20° and 760 mm., *i.e.* about 0.0054 g., are displaced by the platinum; while the weight of the air displaced by 100 grams of brass is 0.0143 g. Hence, the weight of brass which exactly counterpoises 100 grams of platinum is $100 + (0.0143 - 0.0054) = 100.0089$ g. *The buoyancy of the air thus produces a sensible effect whenever the volume of the load differs materially from the volume of the weights.*[1]

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[1] To eliminate the buoyancy correction due to variations in temperature and pressure during the same experiment, it is customary, in weighing bulky glass apparatus (potash bulbs, etc.), to use a similar piece of apparatus as a counterpoise.

The arithmetic of the above calculation is summarized in the formula :

$$\text{Corrected weight} = w + \omega \left(\frac{w}{s} - \frac{w}{s_1} \right)$$

in which w represents the apparent weight of the object; s, the specific gravity of the object; s_1, the specific gravity of the weights; and ω, the weight of a cubic centimeter of air under the conditions prevailing at the time of the experiment.

To illustrate the effect of the buoyancy of air on the different substances usually weighed in clay analyses, the following table may be quoted :

SUBSTANCE WEIGHED	SPECIFIC GRAVITY	ERROR PER GRAM OF SUBSTANCE WEIGHED	
		With Brass Weights	With Platinum Weights
Clay	2.55	0.0003	0.0004
Silica	2.23	0.0004	0.0005
Aluminum oxide	3.85	0.0002	0.0003
Ferric oxide	5.12	0.0001	0.0002
Magnesium pyrophosphate .	2.40	0.0003	0.0004
Calcium oxide	2.90	0.0003	0.0004
Potassium chloride	1.99	0.0004	0.0006
Sodium chloride	2.13	0.0004	0.0005
Potassium chloroplatinate .	3.34	0.0002	0.0003

In ordinary analytical operations we have to deal with *differences* in weight, and with *ratios*, not with absolute weights. When the amount of a precipitate is determined from the difference in the weight of an empty crucible and of the crucible plus the precipitate, the buoyancy correction is not needed for precipitates with a specific gravity near that of the substance undergoing analysis. If, however, the specific gravities are widely separated, it may be worth while to correct for buoyancy. For instance, since the specific gravities of pyrites and barium sulphate are nearly equal, it would be a waste of time to correct for buoyancy in determining sulphur in a sample of pyrites.

On the other hand, in standardizing a solution of silver nitrate by precipitating silver chloride from a specific *weight* of the solution, the buoyancy of air may affect the result by $\frac{1}{10}$ of one per cent.

Summary. The foregoing discussion serves to show that, in work involving delicate measurements, it is always advisable to make an estimate of the influence of the various sources of error on the final result. These errors can only be neglected when their effect is small in comparison with the error derived from other sources. The chief sources of error commonly introduced in the balance room are those arising from: (1) variations in the zero-point of the balance; (2) inconsistent weights; (3) inequalities in length in the beam arms; and (4) the buoyancy of the air. In weighings making any pretense to " accuracy to the $\frac{1}{10}$ milligram," the following points should be noted:

(1) The zero-point of the unloaded balance should be determined and made use of in each weighing.

(2) The weights should be calibrated, and periodically checked for consistency among themselves.

(3) The errors due to inequality in length in the beam arms can be neglected in ordinary analytical work.

(4) The correction of the weighings for the buoyancy of air is necessary when the determination involves the weighing of substances with appreciably different specific gravities.[1]

II. PRECIPITATION

Qualities Desirable in Precipitates Which Are to be Used in Gravimetric Determinations. Precipitation is made use of more often than any other means for the separation of inorganic substances. But, in carrying out such separations, precipitates should conform as nearly as possible to the following ideal specifications: (1) The precipitate should be insoluble in the

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[1] In general analytical work this correction can almost always be neglected, since the resulting error is usually overshadowed by the errors associated with the preparation of the precipitates for the balance.

mother liquid, and also in the wash liquid to be used; (2) it should be compact, easy to filter and wash; (3) it should be a pure chemical substance of known percentage composition; and (4) it should either be stable and non-volatile on heating, or it should yield upon ignition a pure, non-volatile substance of known composition. The last two conditions are of especial importance if the precipitate is the substance finally to be weighed. Moreover, other things being equal, it is conducive to accuracy if a precipitate can be obtained which contains a low percentage of the substance under investigation (cf. Part IV, Problem 46).

But few processes satisfy all these requirements, and in the case of any analytical process it is important to know what conditions favor and what conditions hinder the separation and purification of a given precipitate. There are a few general principles of such wide applicability that they should be constantly borne in mind. Their discussion follows.

Colloidal and Fine-grained Precipitates. Finely divided precipitates, such as newly precipitated silver chloride, barium sulphate, calcium oxalate, etc., are particularly liable to pass through the filter; furthermore, they tend in large measure to stop up the pores of the filter, and thus to increase the time required for filtration and washing. Hence, the analyst employs various artifices in order to enlarge the size of the particles.

(1) The grain size can frequently be increased by allowing the fine grains which originally separate to digest in the precipitation liquid. This change is more rapid in the hot, than in the cold, mother liquid. In the case of crystalline substances, it often happens that the finer grains, which (owing to differences in surface tension) are somewhat more soluble than the coarser ones, redissolve; and since the solution is then supersaturated in respect to the coarser grains, these are augmented in size by the surface deposition of the material furnished by the finer grains.

The boiling of liquids containing colloidal substances frequently leads to the flocculation of a large number of fine particles into a smaller number of coarser aggregates.

(2) Precipitates produced in hot solutions are often coarser-grained than if produced in cold solutions. From what has just been said, the reasons for this fact will be apparent.

(3) The flocculation of a precipitate which separates in a colloidal condition is frequently caused by the salts present in the mother liquid. When these salts have been almost removed, during the washing, the colloidal precipitate is apt to be deflocculated, and it may then give a turbid filtrate, or become so slimy as to be almost impermeable to the wash liquid. In such cases it is necessary to wash the precipitate either with boiling water, or, better, with the solution of an electrolyte which will prevent the deflocculation of the precipitate, and which can be easily removed by drying or ignition. Sometimes dilute acids can be used, but usually, for obvious reasons, we have to depend upon volatile ammonium salts.

The Contamination of Precipitates. Finally, it should be noted that the finer the grain of the precipitate, the greater will be the quantity of contaminating salts likely to be retained by the wet precipitate. The salts appear to be retained by a kind of surface attraction, called adsorption,[1] and, since fine-grained precipitates expose a larger surface of separation between the solid and the liquid phases, and also because of their compactness, the fine grained precipitates are more difficult to wash clean than those of coarser texture. Colloidal gelatinous precipitates like ferric and aluminum hydroxides are in an extremely fine state of subdivision, and, in consequence, they are most difficult to wash clean.

In addition to their tendency to be contaminated by the adsorption of salts, precipitates are also frequently liable to contamination, owing to the formation during precipitation of

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[1] But see "The Contamination of Precipitates in Gravimetric Analysis," G. McP. Smith : Journal of the American Chemical Society, vol. *39*, pp. 1152–73 (1917).

more or less stable insoluble complexes (and, in rare cases, possibly, to the carrying down of foreign substances by the precipitate in a state of solid solution). These impurities, in whatever form they may be present, cannot be completely removed by washing, and the wash water will frequently fail to show any indication of the impurities which are still present in the precipitate.

It is therefore often advisable to redissolve the precipitate, and to repeat the precipitation. The objectionable impurity divides itself in a more or less definite concentration ratio between the precipitate and the mother liquid. A relatively large amount may be retained by the precipitate in the first precipitation, but in a second precipitation, when only that amount of salt retained by the first precipitate is in solution, the division of the undesirable substance between the precipitate and the solution in the given concentration ratio means that a much smaller quantity of impurity will be retained by the second precipitate. Repeated precipitations will, in general, soon carry the amount of impurity outside the range of the balance; but, in carrying out such operations, the solubility relations of the precipitate itself should never be left out of consideration.

The Theory of Precipitation. *Reversible Reactions.* The reactions which are made use of in analytical chemistry belong for the most part to the reversible type. Instead of running to completion, the system may take up a state of equilibrium between the initial stage and that of the completed reaction, and a certain quantity of the substance under investigation is apt to escape our notice. This is especially true in many reactions involving precipitation, neutralization, oxidation, etc.

Furthermore, many reactions are more or less influenced by the presence of certain substances, and it is obvious that a thorough knowledge of the processes which take place in such cases will be of the greatest service to the analytical chemist.

Therefore, it is of primary importance in analytical chemistry to study each process thoroughly in detail, with the object of finding out and understanding the conditions which will be most favorable

for the practical completion of each and every reaction involved in the process.

Indispensable guides for such studies are found in the ionic theory and the law of mass action. It is taken for granted that, at this point, the student is already sufficiently familiar with the qualitative conception of ionization.

Degree of Ionization. In a dilute aqueous salt solution, the greater,[1] and by far the most active, portion of the salt is almost invariably ionic. But with acids and bases there is a wider range, and of these a larger number are less highly ionized; but even here the ions are nearly always much more active than the non-ionized molecules. The acids and bases that are commonly called "strong" are highly ionized, *i.e.* their solutions are especially active as acids or bases because they contain high hydrogen, or hydroxide-ion, concentrations.

Composition of the Ions. It is usual to assume the simplest possible compositions for the ions formed upon the dissociation of any given electrolyte. A more careful study of the subject, however, shows that the ionization of even simple electrolytes may be a very complicated process. It is known, for example, that sulphuric acid contains ions of the formula HSO_4^-, in addition to SO_4^{--} ions, and that phosphoric acid yields ions of the formulas $H_2PO_4^-$, HPO_4^{--}, and PO_4^{---}. All of these are probably more or less highly hydrated; even hydrogen and hydroxide ions are supposed to be hydrated in aqueous solution. Further, many metallic ions show a decided tendency to exist in combination with certain molecules and radicals, as OH_2, OH, NH_3, NH_2, CN, C_2O_4, PO_4, Cl, etc.; but in very dilute solutions these complexes are apt to be more or less highly dissociated into their constituents.

The Law of Mass Action as Applied to Ionic Equilibria. In aqueous solution, acetic acid is supposed to ionize as follows:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-.$$
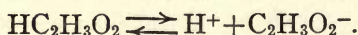
[1] Noteworthy exceptions are mercuric chloride and cyanide, lead acetate, and a few others.

The quantity of the molecular acid that is ionized per unit of time in a given volume of the solution is proportional to the concentration of the non-ionized molecules, $C_{HC_2H_3O_2}$, while the quantity of the molecular acid that is simultaneously formed by the union of the ions depends upon the frequency of the encounters of the two kinds of ions, which in turn is proportional to the product of their concentrations, $C_{H^+} \times C_{C_2H_3O_2^-}$.

The speeds of the respective actions will therefore be

$$S_1 = C_{HC_2H_3O_2} \times F_1 \text{ and } S_2 = C_{H^+} \times C_{C_2H_3O_2^-} \times F_2,$$

in which F_1 represents the intrinsic tendency of $HC_2H_3O_2$ to ionize, and F_2 that of H^+ and $C_2H_3O_2^-$ to combine.

When equal amounts of material are being transformed each way, *i.e.* at equilibrium, $S_1 = S_2$, and therefore

$$C_{HC_2H_3O_2} \times F_1 = C_{H^+} \times C_{C_2H_3O_2^-} \times F_2,$$

or
$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = \frac{F_1}{F_2} = k. \tag{1}$$

$\frac{F_1}{F_2}$, being the ratio of two constants, is constant; and the value, k, of this ratio of the affinities driving the opposed actions is called the *affinity constant* of the reversible reaction. At any given temperature, provided the solution is dilute, the numerical value of k remains the same no matter what the total concentration of the solution may be.[1] In the case of acetic acid, for example, the following figures have been obtained, at 18°, from conductivity determinations.

TOTAL MOLAL CONCENTRATION OF ACID	PROPORTION IONIZED	MOLAL CONCENTRATION OF H+ AND OF Ac− (C_{H^+} AND $C_{C_2H_3O_2^-}$)	MOLAL CONCENTRATION OF HAc ($C_{HC_2H_3O_2}$)
1.000	0.0041	0.0041	1.000−0.0041
0.1000	0.0130	0.00130	0.1000−0.00130
0.0100	0.0407	0.000407	0.01000−0.000407

[1] When data such as the following are applied to cases of soluble, highly ionized substances, the k-values so obtained for any given compound are usually far from constant. The general conclusions arrived at through the application of such data are, however, as a rule, not invalidated by this fact.

Substituting these figures in equation (1) above, we get:

$$\frac{(0.0041)^2}{0.996} = 0.0000169; \quad \frac{(0.0013)^2}{0.0987} = 0.0000171;$$

and $\quad \dfrac{(0.000407)^2}{0.00959} = 0.0000172.$

It is seen that, although the third solution is a hundred times more dilute than the first, and although the degree of ionization has increased tenfold, the value of k is the same in both cases.

The Common-Ion Effect. When, through the presence of two substances which furnish an ion in common, the concentrations of the positive and negative ions of an ionogen are unequal, the law of mass action still holds.

Let us imagine, for example, that, by mixing equal volumes of the double-molal solutions, a solution is obtained which is uni-molal in respect to acetic acid and also to sodium acetate. Let us further suppose that the equilibria which exist in the mixture have been established in two separate stages, as follows: (1) that the concentrations of each undissociated compound and its ions have changed from those which exist in a double-molal, to those which exist in a uni-molal solution of that compound; and (2) that the concentrations of all the substances present have changed from those which exist in the separate uni-molal solutions of the compounds, to those which exist in the mixture which is uni-molal in respect to each compound. Let us now consider this latter stage in detail.

In uni-molal solution, sodium acetate is 0.53 ionized, while acetic acid at that concentration is only 0.004 ionized. Each compound furnishes acetate ions, and the acetate ions present are all available, either for union with sodium ions, or for union with hydrogen ions. Initially, therefore, in the case of the sodium acetate, we have $\dfrac{0.53 \times 0.534}{0.47} > k_1$, instead of $\dfrac{0.53 \times 0.53}{0.47} = k_1$; but the two expressions are so nearly identical that we see at a glance that the ionic equilibrium of the salt will not be

affected appreciably by the presence of the acid. In the case of the acetic acid, however, we have the initial relationship, $\frac{0.004 \times 0.534}{0.996} = 133 \, k$, instead of $\frac{0.004 \times 0.004}{0.996} = k$. Since, at equilibrium, the fraction $\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}}$ remains constant, and since, owing to the low H^+-ion concentration, $C_{HC_2H_3O_2}$ cannot be increased appreciably, nor $C_{C_2H_3O_2^-}$ be appreciably diminished, by the formation of the molecular acid, it follows that the value of C_{H^+} must be lowered to about $\frac{1}{130}$ of its initial magnitude. That is to say, the sodium acetate in this solution diminishes the hydrogen-ion concentration from 0.004 to about 0.00003.

The student should especially note that the concentration of a given ion can be lowered in this way to a value approximating zero *only when that ion unites with an ion added to form a substance which is insoluble or which by nature has only a very slight tendency to dissociate.* We might add sodium chloride in the hope of repressing the ionization of hydrochloric acid; but, since both compounds ionize highly, we should obtain no appreciable effect. If, however, we add sodium acetate in excess to hydrochloric acid, we can obtain a solution which is as weakly acid as the one discussed above.[1]

The Solubility Product. One of the commonest and most interesting applications of the law of mass action is met with in connection with the precipitation and solution of relatively insoluble salts.

Every substance possesses, when immersed in a liquid, a certain *solution-tension,* by which is meant an expansive force which tends to drive particles of the substance outward into the liquid. These particles move in every direction, and consequently some of them return to the solid and reattach them-

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[1] For example, 1 mol of HCl + 2 mols of $NaC_2H_3O_2$, in a volume of 1 liter, give a solution which is uni-molal in respect to acetic acid, to sodium acetate, and to sodium chloride. The hydrogen-ion concentration of this solution would also approximate 0.00003.

selves to it.   This occurs the more and more frequently, as the concentration of the particles in the liquid increases, until, finally, a stage is reached at which the number of particles leaving the solid per unit of time is equal to the number deposited upon it.   When the entire liquid is equally charged with dissolved particles, the liquid immediately surrounding the solid will lose none by diffusion, and a condition of equilibrium will be established.   At any given temperature, the quantity of dissolved solute will remain thereafter unchanged, no matter how long the materials are left in contact.   It is at this point that the solution is said to be saturated with the dissolved substance.

In the case of silver bromate in water, we have the following scheme of equilibria :

$$AgBrO_3 \rightleftharpoons AgBrO_3 \rightleftharpoons Ag^+ + BrO_3^-$$
$$(solid) \qquad (dissolved)$$
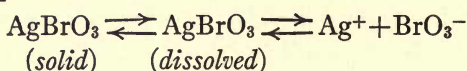
The solid $AgBrO_3$ molecules tend to enter the solution, while at the same time dissolved $AgBrO_3$ molecules tend to come out of solution, and the solution is saturated when these tendencies produce equal effects.   The ions themselves (and any foreign materials present) are not supposed to take any *direct* part in the equilibrium which controls solubility.   That is, *in solutions saturated at a given temperature by a given solute, the concentration of the non-ionized molecules will be constant no matter what other substances may be present, provided that the quantities of all the dissolved substances are not sufficient to alter the nature of the solvent.*

The total solubility of an ionogen, as we ordinarily use the term, is made up of a molecular and an ionic part.   The quantity of the latter does not remain constant when a foreign substance giving a common ion is added to the solution.   In a solution of silver bromate, for example, we have the mathematical relationship :

$$\frac{(Ag^+) \times (BrO_3^-)}{(AgBrO_3)} = k, \text{ or } (Ag^+) \times (BrO_3^-) = k \times (AgBrO_3).$$

But, since, in the special case of a solution which is saturated with the salt at a given temperature, the concentration of the non-

ionized molecules, $(AgBrO_3)$, remains constant, it follows that the product, $k \times (AgBrO_3)$, also remains constant, or that *in a saturated solution of a given slightly soluble ionogen the product of the concentrations of its ions is constant*. This product is called the solubility product, because the two separate values jointly determine the magnitude of the total solubility of the ionogen. The concentration of the non-ionized molecules cannot be diminished, but the ionic part of the solute may become vanishingly small if the concentration of the common ion is made great as compared with that of the other ion of the solute. The relationships which exist in the case of silver bromate are illustrated in the following table, where it will be seen that the experimental values agree remarkably well with the calculated ones.

SOLUBILITY OF $AgBrO_3$ IN MOLS PER LITER

Mols per Liter of Common-ion Salt Added	Solubility Found		Solubility Calc.
	Addition of Silver Nitrate	Addition of Potassium Bromate	(Addition of either Salt)
0	0.00810	0.00810	————
0.00850	0.00510	0.00519	0.00504
0.0346	0.00216	0.00227	0.00206

The theory of the precipitation and solution of *slightly soluble* ionogens may be summed up as follows: [1]

[1] That is, of uni-univalent ionogens. In other cases, the solubility product would often contain ion-concentrations raised to the second, third, etc., powers; but in reality the question is very much complicated by interfering reactions. Thus, in the case of $PbCl_2$, if NaCl is added to the saturated solution, some $PbCl_2$ will be precipitated in accordance with the theory; but the addition of $Pb(NO_3)_2$ actually increases the solubility of the $PbCl_2$. This is probably because of the formation of complexes, or of intermediate ions, such as $PbCl^-$, or of both, whereby the addition of the salt giving the common bivalent ion may not only fail to increase the concentration of the bivalent ion, but may even lower that of the univalent ion. At any rate, enough is known to indicate that the theory may not be so much at fault as we ourselves, in our lack of methods for finding out just what ions and complexes are present in such solutions, and in what quantities.

If the product of the concentrations of any pair of ions in a solution is made to exceed the solubility product of the ionogen formed by their union, the latter will be precipitated until the ion-concentration product has been reduced to its solubility-product value. And conversely, *if the ion-concentration product of any pair of ions in a solution is made less than the solubility product of the ionogen formed by their union, the latter will, if present in sufficient excess, continue to dissolve until the ion-concentration product has been increased to its solubility-product value.*

III. FILTRATION AND THE WASHING OF PRECIPITATES

The purpose of filtration is to separate a solid from a liquid in which it is suspended. This is effected by causing the liquid to pass through a porous medium compact enough to retain the solid. The most important media in use are filter paper, asbestos pulp, and platinum sponge.

The Selection and Use of Paper Filters. Three qualities which are desirable in a filter are: (1) porosity, to insure rapid filtration; (2) sufficient compactness, to insure complete retention of the precipitate; and (3) low amount of ash. In quantitative work, only filters should be used which have been treated with hydrochloric and hydrofluoric acids, and which, on incineration, leave a small and definitely known weight of ash. Such filters are readily obtainable in the market.

Rapid (porous) filters should be used for all precipitates which do not readily pass through the paper; the slow, compact papers should be used only when necessary. A tremendous amount of time is consumed, often wasted, in the filtration and washing of precipitates.

The size of the filter paper should be determined by the magnitude of the precipitate, and not by the volume of the liquid to be filtered. A precipitate should not fill the paper more than half full, but if too large a paper is used, time is wasted in washing the filter. *The filter, as well as the precipitate, has the property of retaining certain salts very tenaciously.*

Funnels should be selected which have an angle of 60°, with a narrow stem about eight inches long. The filter should be accurately folded to fit the funnel, and the top of the filter should be at least one half centimeter below the edge of the funnel. On no account should the paper project beyond the edge of the funnel.

Place the filter in the funnel, wet it, and carefully bed it against the walls of the funnel. When the filter is filled with distilled water, the stem of the funnel should fill with a column of water,[1] and air should not pass between the funnel and the paper as the latter empties. When the filter is properly bedded, water should flow through it quickly, and filtration will usually proceed quite rapidly; at any rate, the paper will then do its best. The liquid at the apex of the filter is under a pressure approximately equal to the weight of a column of water of the same diameter as the bore of the stem and of a height equal to the length of the stem plus the depth of liquid in the filter.

When paper filters are employed, the use of a vacuum pump to promote filtration is of doubtful advantage in quantitative analysis. The increased tendency of precipitates to pass through the filter more than offsets the possible gain in time. Whenever suction is applied, a more compact paper should be used, or the point of the filter should be supported by a perforated platinum cone.

The vessel used to receive the initial filtrate should invariably be replaced by a clean one, properly labeled, before the washing of a precipitate is begun. Precipitates which at first show no tendency to pass through the filter may enter into colloidal solution as the washing proceeds. The advantage gained in such an instance by having removed the first filtrate is obvious.

The precipitate is generally allowed to settle before filtration. The clear liquid should not be poured directly on to the filter,

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[1] If this fails to take place, either the stem of the funnel is too wide, or it is not free from grease. The latter can be removed by means of warm sulphuric acid-dichromate cleaning solution.

but down a glass rod, from which the stream should be directed towards the side, not the center of the filter paper. The receiving vessel for the filtrate should be placed so that the liquid from the funnel will run down its side; otherwise there is danger of loss by splashing. As far as possible, the precipitate itself should be kept in the precipitation vessel.

Much time can generally be saved by washing the precipitate by decantation, *i.e.* by adding to it successive portions of wash liquid, allowing the precipitate each time to settle, and decanting the clear supernatant liquid through the filter, without unduly disturbing the precipitate. This procedure is especially advantageous in the case of precipitates which tend to clog the pores of the filter. Finally the precipitate may be transferred to the filter, and the washing completed there.

It will always be found that small portions of the precipitate adhere to the walls and bottom of the containing vessel. These can be rubbed loose by means of a so-called "*policeman*," — a piece of soft rubber tubing *tightly* fitted on the end of a glass rod. Pieces of rubber tubing with closed ends are sold for the purpose. *These rubber-tipped rods should be used only for the above-mentioned purpose; they should never be allowed to stand in analytical solutions, nor should they be used as ordinary stirring rods.*

Precipitates should never be allowed to dry before they have been completely washed. They are likely to shrink and crack, and, on further washing, the liquid will pass through these channels only; this is especially true of gelatinous precipitates.

Every original filtrate must be properly tested to insure complete precipitation, and the wash waters also must be examined. It is useless, however, to test the latter until several washings have been made. Only a few drops should be taken if the filtrate is to be used for a subsequent determination; but when the washing is nearly finished, at least 2 or 3 cc. should be used. *The necessity of making these tests cannot be too strongly impressed upon the student; and no exception should ever be made.*

Wash Bottles. Wash bottles, for distilled water, should consist of flasks of about 500 cc. capacity which are provided with rubber stoppers and with tubes gracefully bent and not too long. The jet should be connected in a flexible manner with the outlet tube by means of a short piece of soft rubber tubing, and should deliver a smooth stream about 1 mm. in diameter. For use with hot water, the neck of the bottle should be wrapped with heavy asbestos twine, or other suitable material. In order to avoid mistakes, wash bottles for other liquids than distilled water should always be plainly labelled.

Gooch's Filtration Crucible. In 1878, F. A. Gooch proposed the separation of certain precipitates by filtration with suction through a mat of asbestos bedded on the perforated bottom of a crucible. The precipitate then could be washed, dried, and weighed in the crucible.

Preparation of the Asbestos. There are several varieties of asbestos in the market, of which the long-fiber " silky " chrysolite asbestos is the best. Rub the asbestos roughly over the surface of a 10-mesh brass sieve, placed in an inverted position on a sheet of paper, until a sufficient quantity has passed through. Shake this up with water, allow most of it to settle, and pour off the very fine particles. Now, digest the pulp on the steam bath for 1 hour with strong hydrochloric acid, in a covered porcelain dish. At the end of this operation, dilute the mixture with water, pour off the liquid through a funnel provided with a platinum filtration cone, and wash the asbestos with hot water, at first by decantation, and finally in the funnel, using gentle suction, until a 5 cc. portion of the filtrate fails to give an opalescence with silver nitrate. Mix the washed asbestos with distilled water and keep it in a bottle ready for use.

Packing the Crucible with Asbestos Felt. Stretch a piece of rubber-band tubing over the upper edges of a cylindrical glass tube, about 3 cm. in diameter and 7 cm. long, which is closed at one end except for an attached stem of suitable size and length to pass through a rubber stopper. The tubing should project

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1.5–2 cm. above the top of the funnel tube. Fit the glass funnel tube into the stopper of a filter bottle, connect the latter with the vacuum pump, and then press into the short projecting end of the rubber tube the Gooch Crucible, so that it fits in an air-tight manner.

Take some of the asbestos suspension referred to above, add water, and stir the mixture. Allow this to settle for some time, pour off the very fine particles, apply a *gentle* suction, and then pour some of the mixture cautiously into the crucible until an even felt of asbestos, not over 1.5 mm. in thickness, is formed. Place a small perforated disk (filter plate) upon the asbestos, and pour just enough more asbestos into the crucible to barely cover the disk. Run water through the crucible until no more asbestos fibers run through, and make sure that the washings are free from chlorides. If the water which has passed through the crucible is held before a bright light, any suspended asbestos fibers can readily be seen. Usually, 250–500 cc. of water will suffice. The perforated filter plate is used to protect the asbestos felt, during the washing and subsequent filtration.

Place the crucible in a small beaker, dry at 120–130° for an hour, cool in a desiccator, and weigh. Heat again, for $\frac{1}{2}$ hour, cool, and again weigh, repeating until the weight is constant within 0.0002 g. The filter is then ready for use.

How to Use the Gooch Crucible. The weighed crucible is re-placed in the funnel, and a gentle suction applied, *after which* the liquid to be filtered may be passed through the crucible, and the precipitate washed as if the crucible were a filter paper and funnel. When pouring liquid into the crucible, hold the stirring rod well down in the crucible, so as not to disturb the asbestos. Always examine the first portions of the filtrate with great care for asbestos fibers, and refilter the liquid if any are visible.

When the precipitate has been washed and the crucible dried, the whole is weighed. The drying and weighing should be repeated, as above, to constant weight. The increase in weight represents the weight of the precipitate.

The same crucible can be used for a number of determinations of the same substance. When the collection of precipitates in the crucible becomes too large, the upper part can be removed, and the crucible used as before. If the felt has been properly prepared, filtration and washing are rapidly accomplished, and this, combined with the possibility of repeatedly using the same filter, is a strong argument in its favor, with any but gelatinous precipitates.

If perforated platinum crucibles are available, which after removal from the funnel, can be fitted into platinum cups, the precipitates can be ignited as in ordinary crucibles. In this case, however, it is better to pack the Gooch crucible with a felt of platinum sponge. In this form, the apparatus is known as a Munroe Crucible.

Sources of Error. It is important to remember that asbestos may absorb appreciable amounts of alkali, not removed by washing, so that, as a rule, solutions containing fixed alkalies should not be filtered through asbestos. Asbestos is also slightly attacked by water and feebly acid solutions; but after the treatment indicated above, there is no real danger from this source. If the felt has been properly prepared, there is no danger of losing asbestos during the filtration and washing, but the liquid which runs through should nevertheless be carefully examined, and refiltered if necessary.

The Theory of Washing Precipitates. The theory of washing precipitates should include the consideration of several factors, among which may be mentioned the phenomena of adsorption (in which the filter also takes part), and the tendency of precipitates to enter the wash liquid in colloidal form. But these factors have been discussed under precipitation. Aside from these considerations, there is the important question concerning the most effective method of washing precipitates.

Let us suppose that a precipitate is to be washed by decantation, and for the sake of simplicity let us assume that neither it nor the filter exercises any physical or chemical action on the

salts dissolved in the mother liquid. The supernatant mother liquid has been decanted as far as possible into the filter, and the latter has been allowed to drain.

Let v cc. be the total volume of solution which remains in contact with the precipitate and filter, and V cc. the volume of wash water added each time; and assume that the latter mixes uniformly with the liquid adhering to the precipitate and filter. Then, upon the addition of V cc. of water, the total volume of liquid is $(V+v)$ cc. Further, let C_0 be the concentration in grams per cubic centimeter of the undesirable salts in the original solution; then the quantity contained in the v cc. left in contact with the precipitate and filter is vC_0 grams. By the addition of V cc. of water, the concentration is reduced to $C_1 = \dfrac{v}{V+v} C_0$, and if this liquid is removed until only v cc. are left, the quantity of undesirable salts present is reduced to $vC_1 = \dfrac{v}{V+v} \cdot vC_0$. A second addition of V cc. of water gives the concentration, $C_2 = \dfrac{v}{V+v} C_1 = \left(\dfrac{v}{V+v}\right)^2 C_0$, and the quantity of salts in the v cc. left on draining is now

$$vC_2 = \frac{v}{V+v} \cdot vC_1 = \left(\frac{v}{V+v}\right)^2 vC_0 ;$$

or, after n washings, the quantity of undesirable salts has been diminished to the value,

$$vC_n = \left(\frac{v}{V+v}\right)^n vC_0.$$

This formula expresses mathematically the self-evident fact that, for a given number of washings, the quantity of undesirable salts left behind will be the smaller, the more completely the precipitate and filter are drained, and the greater the volume of the wash water that is added each time. The formula enables us, however, to find the answer to a less simple question; viz., What is the most efficient method of washing a precipitate with

a given amount of wash liquid? Suppose, for example, we wish to use only 150 cc. of wash liquid : is it better to wash six times with 25 cc. portions, or to wash 10 times with 15 cc. portions? Let us assume that $C_0 = 0.1$ g. per cubic centimeter, and that $v = 5$ cc.; then, in the two cases, the quantities of undesirable salts left behind will be $(\frac{5}{30})^6 \times 0.5 = 0.0000107$ g., and $(\frac{5}{20})^{10} \times 0.5$ $= 0.00000047$ g., respectively. Disregarding adsorption, which greatly decreases the efficiency of washing, ten washings with 15 cc. portions are 23 times as efficient as six washings with 25 cc. portions. Both methods of procedure will require approximately equal intervals of time, since, in either case, 150 cc. of liquid must run through the filter. *It is much better to wash a precipitate many times with small portions of liquid, than a few times with larger portions. Each portion of wash liquid should be removed as far as possible by decantation and drainage, before the addition of a fresh portion.*

Another factor to be considered is the temperature of the solution to be filtered. Since the rate of flow of a liquid through a filter depends largely upon the viscosity of the liquid, and since the viscosity of water at 100° is only one sixth that of water at 0°, it is well to filter and wash at a high temperature, unless there is good reason to the contrary.

Finally, in washing a precipitate on a paper filter, great care must be taken to wash the filter itself. Soluble salts are tenaciously held back at the upper edges of the paper, and therefore this part of the filter should receive especial attention. *It is best to fill the filter each time, and, before refilling, to allow it to drain completely.* This is a strong argument in favor of filters which are not too large.

IV. THE DRYING AND IGNITION OF PRECIPITATES

Drying Ovens. There are on the market many types of drying ovens, heated by gas, by steam pipes, or by electricity, in which the temperature may be more or less accu-

rately controlled. The oven consists essentially of a drying chamber, through which there is provided a slow circulation of hot air.

A precipitate is dried on the filter by placing the funnel containing both in a drying oven, at 90–100°, and leaving it there for a sufficient time. The funnel should be covered with a sheet of common filter paper, fastened in place by crimping its edges over those of the funnel. If the precipitate is suitable for weighing without ignition, *e.g.* silver chloride in a Gooch crucible, it should be dried to constant weight at a temperature considerably above the boiling point of water (in this case, at 120–130°), in order to remove the last traces of moisture from the filter as well as from the precipitate. (Before it is used, the packed Gooch crucible should, of course, be dried to constant weight at the same temperature.)

Many precipitates may, under proper precautions, be ignited without previous drying in an oven. But if such precipitates can be dried over night, or otherwise, without loss of time to the analyst, it is well to submit them to this process.

The precipitate, with the filter folded over it, is placed at the bottom of the crucible, and the latter is supported, on a triangle, so far above the small flame of a burner as to preclude the violent escape of steam. When the filter and contents are dry, the open crucible is tilted on its side, and the heat slightly increased until the filter chars; the heating is then continued at this rate until the gases from the dry distillation of the paper have been completely expelled without taking fire. In this way, no material will be lost owing to strong draughts caused within the crucible by burning gases.

During the dry distillation of the paper, the flame should be placed near the mouth of the crucible; but afterwards it should be well at the base of the inclined crucible, to allow a ready access of air. After the filter has been freed from volatile matter, the crucible should be heated to redness until the ignition is complete.

Some precipitates are reduced or otherwise affected by contact with hot carbon or reducing gases from the filter paper; *e.g.* silver chloride, lead sulphate, etc. are reduced to metal. Since, however, these metals are volatile only at very high temperatures, there is no loss in their case, and the metal can by suitable treatment be transformed quantitatively into the original compound. In such cases it is advisable to separate the precipitate as far as possible from the filter, and then to ignite the latter. The small quantity of reduced metal is moistened with a few drops of nitric acid, and the resulting nitrate converted into silver chloride with hydrochloric acid, or into lead sulphate with sulphuric acid, and the excess of acid expelled by cautiously heating the crucible. The bulk of the precipitate is then added, and the whole ignited.

Unless specially directed, precipitates should not be heated over the blast lamp.

Desiccators. After an object has been dried and ignited, it must be permitted to cool before it can be weighed with accuracy. In order to protect it from contamination with moisture, carbon dioxide, etc., it should invariably be allowed to cool in a desiccator.

For general analytical work, desiccators should be charged with fragments of fused, anhydrous calcium chloride, some distance above which is placed a porcelain plate provided with holes of a size suitable for the reception of crucibles. In order to give the cover of the desiccator an air-tight fit, the ground-glass contact surfaces should be thinly coated with vaseline or some similar substance.[1]

Desiccators should never be left uncovered. The dehydrating agent is intended to keep the air inside the desiccator dry; it rapidly loses its efficiency if exposed to the outside air. If the lumps of calcium chloride tend to stick together, the charge should be renewed.

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[1] A mixture made by melting together equal parts of vaseline and beeswax is very suitable.

Pumice moistened with concentrated sulphuric acid is sometimes used instead of calcium chloride.

Crucibles. The most commonly used crucibles are of high grade porcelain. They withstand very high temperatures without appreciable change of weight, and they are comparatively cheap in price. They cannot be used for fusions because most fluxes, particularly those of a basic nature, attack the glaze as well as the porcelain itself. Even in the ignition of non-basic precipitates, in spite of the most careful washing, traces of fusible materials always remain with the precipitate, and these in time destroy the glaze. After the lining is thus roughened it is difficult to clean, and the crucible is unsuitable for use.

Crucibles more or less suitable for the ignition of precipitates are also made of alundum, and of fused silica.

Crucibles of platinum are very desirable for ignitions; and for many fusions they are essential. Platinum melts at about 1770° and does not soften enough to preclude its use at temperatures slightly below its melting point. It is soluble in liquids containing free chlorine, such as nitrate-chloride mixtures of acid reaction, and to a lesser degree in acid ferric chloride solutions. Care must be taken to prevent injury to platinum vessels, or the introduction of platinum into solutions, by a disregard of these facts.

Platinum easily alloys with most metals, and for that reason it should not ordinarily be heated in contact with metals, or with compounds of easily reducible metals, — never, if carbon or reducing gases are also present. When heated for a long time in contact with carbon, platinum slowly takes up the latter and becomes brittle; therefore, the crucible should never be heated in a reducing flame. The flame should be carefully adjusted so that the tip of the inner cone is *below* the bottom of the crucible, and a flame showing yellow must never be used. Compounds of phosphorus or arsenic must not be heated under reducing conditions, since the free elements, as well as phosphides and

arsenides, render platinum brittle and lower its melting point. "Unknown" substances should never be heated in platinum vessels.

Platinum ware should always be kept bright and clean. For this purpose it should be frequently polished with fine sea sand or with precipitated silica. These remove most impurities, and polish the platinum without serious loss. The fusion of potassium bisulphate in the vessel is a good method for cleaning the badly tarnished inside. The bisulphate should be poured out of the crucible while still liquid; for if it has been strongly heated, the melt (pyrosulphate) is apt to expand so rapidly on cooling as to burst the crucible.

Never heat the platinum crucible or dish in contact with iron or metals other than platinum, nor place hot platinum in contact with foreign metals. Use nothing but pipeclay, quartz, or platinum triangles, and platinum-shod tongs.[1]

V. THE EVAPORATION OF LIQUIDS

The greatest care must be taken to prevent loss of material during processes of solution and evaporation, either from the evolution of gas, from too violent ebullition, or from evaporation

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[1] Modern platinum ware is often inferior in quality to that on the market some years ago, and the cause has been the subject of special inquiry by a committee of the American Chemical Society. The main objections are: "(1) Undue loss of weight on ignition; (2) undue loss on acid treatment, especially after strong ignition; (3) unsightly appearance of the surface after strong ignition, especially after the initial stages of heating; (4) adhesion of crucibles and dishes to triangles, sometimes to such an extent as to leave indentations on the vessel at the points of contact with the triangle, even when complete cooling has been reached before the two are separated; (5) alkalinity of the surface of the ware after strong ignition; (6) blistering; and (7) development of cracks after continued heating." It is the general opinion that the trouble arises from the working of scrap platinum into chemical ware. The main difficulties here mentioned are not characteristic of platinum ware from some of the best manufacturers.

The committee recommends that purchasers specify that platinum ware must show no marked uneven discoloration on heating, must give no test for iron after heating for two hours, and that the rate of loss per hour at 1100° over a period of four hours shall not exceed 0.2 mg.

nearly to dryness accompanied by spattering or by the " crawling " of salts over the edge of the vessel. In order to prevent mechanical losses, solutions in which gases are being evolved, or which are to be boiled on the hot plate, should invariably be covered. And liquids which contain suspended matter (precipitates) should always be cautiously heated, since the presence of solid matter frequently occasions violent " bumping " which may lead to mechanical losses or to the destruction of the vessel.

The evaporation of aqueous solutions rarely requires the use of temperatures above 100°. Temperatures somewhat below this point, but sufficient for the evaporation of most aqueous solutions, are best attained by the use of the steam bath, which has the advantage of keeping the solutions at a temperature below that at which mechanical losses are to be feared.

Evaporations should not be attempted in tall, narrow vessels, but should be carried out in low, wide-mouthed dishes or casseroles : it is obvious that evaporation is promoted by the exposure of a large surface of liquid to the air. In evaporations on the steam bath, a watch glass should be supported above the casserole or dish by means of a glass triangle or other suitable device.

If a large volume of liquid is to be evaporated, it is not necessary that the vessel should contain it all at once. Fresh portions of the liquid may be added, from time to time, as the volume of that in the vessel is reduced by evaporation.

Liquids should never be transferred from one vessel to another, nor to a filter, without the aid of a stirring rod held firmly against the lip or side of the containing vessel. In order to prevent the loss of liquid by running down on the outside of the vessel, a *very thin* coating of vaseline, applied with the finger to the outside edge of the vessel, will suffice. If the vessel is provided with a lip, this is usually unnecessary.

As few transfers of liquid as possible from one vessel to another should be made during an analysis. In such transfers, the solu-

tion must, of course, be quantitatively washed out. This can be accomplished better by the use of successive small portions of wash water, say of 5–10 cc. each, than by the addition of a few larger portions which unnecessarily increase the volume of the solution and lead to loss of time in subsequent filtrations or evaporations.

VI. THE VOLUMETRIC MEASUREMENT OF LIQUIDS[1]

Measurements with a good balance and weights can often be made with a precision even greater than is necessary for general analytical work. But, as has been intimated, the errors involved in the preparation of a troublesome precipitate for weighing may impair the value of an exact weighing. Although the measurement of volume, in volumetric analysis, is not apt to be so precise and reliable as the measurement of weight,[2] yet the results of volumetric processes, based on suitable reactions, are frequently more trustworthy than those of gravimetric processes, because the volumetric process for the determination of the substance is less liable to error. With proper precautions many volumetric processes yield excellent results; and, especially in technical work, where time is an essential factor, volumetric processes are very often used in preference to gravimetric. In order, however, that dangerous errors may be eliminated in volumetric work, it is of great importance that the analyst should have a clear idea of the precautions necessary for the attainment of a high degree of accuracy.

[1] For more detailed information on this subject, see *Bulletin of the Bureau of Standards*, Vol. 4, pp. 553–601 (1908).

[2] Even this difficulty can be obviated by the use of *weight burettes; i.e.* of burettes of such construction as to be readily weighable both before and after the removal of the quantity of solution required for the completion of the given reaction. The difference gives the weight of solution required, and, provided the solution has been standardized by the same method, the quantity of the substance under investigation can be readily calculated. In this way, if based on suitable reactions, exceedingly exact determinations can be executed. (A similar weight burette should always be used as a counterpoise.)

Volumetric Apparatus. The exact measurement of liquid volumes necessitates the use of certain special forms of apparatus, the most important of which will now be described.

Burettes are graduated glass tubes of uniform, small diameter, designed to measure variable amounts of liquids delivered by them when supported in a vertical position. The outflow of the liquid is controlled either by a glass stopcock or by means of a rubber joint which connects the end of the tube with a glass nozzle, and which is provided with a pinchcock or other suitable device. The former require the use of some lubricant, such as vaseline, to permit easy control of the outflow, and the latter have the disadvantage that the rubber connection is acted upon to some extent by certain solutions, which in consequence are apt to experience a change in concentration; *e.g.* rubber stopcocks should never be used with permanganate or iodine solutions. For accurate work, 50 cc. burettes should be graduated to 0.1 cc. and 25 cc. and 30 cc. burettes to 0.05 cc., and the graduation marks should be separated by at least 1 mm.

Transfer Pipettes are tubes of much smaller bore than burettes, designed to deliver specific volumes of liquid. They are provided with an enlargement at the center, which greatly reduces the length required, and with a single mark on the upper length, which indicates the point to which they must be filled in order to deliver the indicated volume of liquid. Pipettes are filled by suction and are allowed to deliver the liquid, while held in a vertical position, by the action of gravity. On account of the smallness of the bore at the point where the reading is made, the pipette may be made to measure liquids with a high degree of accuracy. However, certain errors of manipulation often render the measurements inexact.

Measuring Flasks are employed for measuring relatively large volumes of liquid in one portion. The neck must be sufficiently small to permit a reading with only a slight percentage error, but large enough to permit filling and emptying without trouble. The neck should also be of uniform bore and

of some margin above and below the mark. For the most accurate work the flask is always graduated for *containing* the amount indicated by the inscription upon it.

Graduated Cylinders are cylindrical glass vessels provided with an enlarged base or foot and with a lip for pouring. They are marked to indicate the varying amounts of liquid which they may contain and are employed for rough measurements only.

Necessary Precautions in the Use of Volumetric Apparatus. In making use of volumetric methods, the following are the most important sources of error; they must be fully reckoned with if the results are to be reliable.

Errors Due to Water in the Apparatus. It is usually necessary to rinse the apparatus with water before using; and the amount of water retained may appreciably change the concentration of the solution measured. The error can be avoided by drying the apparatus before use, or, more conveniently, by rinsing it out with several small portions of the solution to be measured, and discarding the washings.

Errors Due to Drainage or Afterflow. When a liquid is permitted to flow somewhat rapidly from a burette, or pipette, small amounts adhere to its inner surface, and gradually flow down and unite with the liquid still remaining in the vessel. In order to avoid errors from this source the rate of outflow must be limited by the size of the outlet, and a sufficient interval must elapse between the time at which the flow from the apparatus is stopped, and at which the reading is made. This interval, unless indicated on the instrument, may be taken as 30 seconds in the case of burettes and 15 seconds in the case of pipettes.

In the case of transfer pipettes, the outlets must be of such size that the free outflow shall last not more than one minute and not less than 15, 20, and 30 seconds respectively, for 5, 10, and 50 cc. pipettes. The rate of outflow of burettes must not be more than three minutes, nor less than 90 and 50 seconds, respectively, for 50 and 30 cc. burettes. Burette and pipette tips should be made with a gradual taper of 2–3 cm.; a sudden

contraction at the orifice is not permitted, and the tip should be well finished.

In filling pipettes and burettes excess liquid adhering to the tip should be removed when completing the filling. In emptying pipettes and burettes, they should be held in a vertical position, and after the continuous unrestricted outflow has ceased the tip should be touched with the wet surface of the receiving vessel, to complete the emptying. *Apparatus must be sufficiently clean to permit uniform wetting of the surface.* (For the preparation of cleaning solution, see the Appendix.)

Errors Due to Parallax. In all apparatus in which the volume is limited by a meniscus, the reading or setting is made, when possible, on the lowest point of the meniscus. Since this point lies at the center of the tube, the error from parallax must be avoided. The method of doing this is to support the tube so that its main axis is vertical, and to hold the eye at such a level that the line of sight makes an angle of 90° with the axis.

In order that the lowest point of the meniscus may be observed, it is well to place a screen of some dark material immediately below the meniscus, which renders the profile of the meniscus dark and clearly visible against a light background. A convenient device for this purpose is a collar-shaped section of black rubber tubing, cut open at one side and of such a size as to clasp the tube firmly.

Errors Due to Variations in Temperature. The volume occupied by a given weight of water, as well as the capacity of the measuring vessel, is dependent upon the temperature; and the error involved in the measurement of the volume of a given mass of water, at any other temperature than the standard one, is due to the joint effect of the changed capacity of the vessel and the changed volume of the liquid.

The coefficient of cubical expension of ordinary glass may be taken to be 0.000025; but the volume change of the water is much greater than that of the glass measuring vessel, and also much less uniform from degree to degree. The factors by

which a volume of water, measured at temperatures ranging from 10–29° in a vessel calibrated for 20° must be multiplied in order to obtain the true volume occupied by the liquid at 20°, are given in the following table:

	TEMPERATURE OF THE WATER				
UNITS TENS	0	1	2	3	4
1	1.00124	1.00117	1.00109	1.00100	1.00089
2	1.00000	0.99981	0.99961	0.99941	0.99919

	TEMPERATURE OF THE WATER				
UNITS TENS	5	6	7	8	9
1	1.00077	1.00064	1.00049	1.00034	1.00018
2	0.99896	0.99873	0.99848	0.99822	0.99798

If the prevailing temperature does not differ by more than, say, 3° from the standard, this correction may ordinarily be omitted. In the case of solutions of 0.2 N concentration, or less, the corrections differ so little from those for pure water that the factors given in the table may be used without appreciable error.

In order to illustrate the use of such factors, let us suppose that, in the standardization of a solution, a burette graduated correctly for 20° is used at an actual temperature of 27°, and that the indicated volume of solution withdrawn is 28.75 cc. Then the true volume at 20° of this quantity of liquid is 28.75 × 0.99848 = 28.70 cc. And, if a determination is later made with this solution at, say, 17°, and the indicated volume used is 28.68 cc., then the true volume at 20° is 28.68 × 1.00049 = 28.70 cc. That is to say, the same quantity of reagent is contained in an apparent volume of 28.75 cc. at 27°, or in an apparent volume of 28.68 cc. at 17°, as is contained in an actual volume of 28.70 cc. of the solution at 20°.[1]

[1] At 27° the *actual volume* of the liquid measured is a shade greater than 28.75 cc., and at 17° it is a shade less than 28.68 cc. The measuring vessel is larger at 27°, and smaller at 17°, than it is at 20°.

Errors due to Different Units of Volume Employed.   Unfortunately, a number of different " liters " have been suggested for use in volumetric analysis. *The normal liter*, that is, the volume occupied by a kilogram of water, weighed in a vacuum and measured at 4°, would manifestly be out of the question if it had to be determined in that way.   The so-called " *Mohr liter* " is the volume occupied by a kilogram of water when weighed in the air with brass weights at a temperature of 17.5°; but this volume varies with the atmospheric conditions.   Other " liters " involving measurements at 15°, 15.5°, or 20° have been suggested by various chemists.

It matters little, in analytical work, which liter is adopted, but *it is of the greatest importance to have the pipettes, burettes, and measuring flasks rigorously consistent with one another.* This matter is serious enough to require especial emphasis, since apparatus, if not specifically ordered, may be supplied by dealers, at different times, graduated according to different systems; and mixed graduations may thus come into the hands of an individual analyst.   As an example of the magnitude of the errors which might thus be introduced, it should be noted that the normal liter is related to the Mohr liter as 1000 : 1002.3.

Much of the graduated apparatus on the market bears no mark by means of which the unit of volume represented can be recognized, and even when this is clearly designated the percentage error represented may be large.   It is not advisable, therefore, to use any piece of graduated apparatus, unless its actual value is well known.

Owing to the great difficulty in measuring directly the relation between cubic capacity and the unit of length, the International Committee of Weights and Measures defines the liter as " the volume occupied by the mass of one kilogram of pure water at its maximum density under normal atmospheric pressure."   This is almost exactly 1000 cc.[1] and for all practical purposes may be regarded as such.

[1] About 1000.029 cc.

It is now customary to use this true liter as the standard, but of course it is out of the question to weigh a kilogram of water at 4° in a vacuum; some convenient temperature — preferably the average working temperature of the laboratory — must be selected, and the necessary corrections made. If a liter flask is marked correctly at 20°, this means that at 20° it will contain a mass of water (998.234 g.) which occupies a volume equal to that occupied by 1000 grams of pure water at 4°. This quantity of water, if weighed with brass weights in air of mean humidity, at 20° and 760 mm., has an apparent weight of 997.18 grams.

The Calibration of Volumetric Apparatus. The weight of brass (brass weights) which will be required to counterbalance one liter of pure water must be calculated from the temperature of the water and the density of the air. The following table indicates, for temperatures of the water (and room) ranging from 15–29°, how many milligrams less than 1000 grams a quantity of water will weigh which is sufficient to fill to the mark a 1-liter flask correctly calibrated for 20°, the weighing being carried out in air of 50 per cent humidity at 760 mm. pressure (unreduced).[1]

UNITS \ TENS	0	1	2	3	4	5	6	7	8	9
1	—	—	—	—	—	1950	2100	2260	2440	2630
2	2820	3030	3240	3470	3710	3960	4210	4480	4760	2620

If such a flask is filled to the mark with water of 22.4°, for example, the water will under the conditions of the table require a counterpoise of 1000−3.332 = 996.668 grams.

The determination of the capacity of a measuring flask is carried out by weighing the water contained in it, while the volume of water delivered by a burette or pipette is determined by weighing this water after its delivery into another vessel.

[1] These values depend upon the specific gravities of the water and the (brass) weights, the density of the air, and the coefficient of cubical expansion of the glass vessel.

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The temperature of the water should be taken before and after the experiment; it is important that it should be the same as the room temperature at the time of the weighing.

In the calibration of a flask, the dry flask is placed upon the right-hand pan of the balance, together with the nominal weight of its capacity, *i.e.* with as many grams as it is supposed to contain cubic centimeters, and then tare material is placed upon the left-hand pan until the balance is brought into equilibrium. The weights are then removed from the right-hand pan, the flask is filled to the mark with water, and weights are added until the balance is again in equilibrium. The nominal capacity weight, minus the additional weight which is required upon the right-hand pan in order to reëstablish equilibrium, is equal to the weight of the water in the flask.

In the case of burettes and pipettes, a covered beaker is placed upon the right-hand pan, together with the nominal weight in grams of the volume to be delivered, after which the balance is brought into equilibrium by the addition of tare material to the left-hand pan. The water is then allowed to run into the beaker, which is replaced upon the right-hand pan. The subsequent procedure is the same as that described above.

The difference between the additional weight required to reëstablish equilibrium and that calculated from the above table indicates directly the error of the vessel. If, for example, it be found necessary, in order to reëstablish equilibrium in the case of a 500-cc. flask filled to the mark with water of 22.4°, to add 1.832 g., instead of the calculated 1.666 g., then it follows that the vessel is 0.166 cc. too small. On the other hand, in testing the 25 cc. segment of a 30-cc. burette, at a temperature of 17°, the additional weight required on the right-hand pan should be $(25 \times 2260) \div 1000 = 57$ mg.; if, instead of this, it be found that an additional weight of 15 mg. is required on the *left-hand* pan, then the 25 cc. segment is 57 mg. $- (-15$ mg.$) = 0.072$ cc. too large.[1]

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[1] This error is too large to be tolerated.

In the calibration and use of burettes, the liquid should in general be allowed to flow from the zero mark to some second level in the burette.

D. THE PREPARATION OF SAMPLES FOR ANALYSIS

It is not easy to give general rules for the preparation of substances for analysis, because it is necessary to proceed differently in different cases. In all cases, however, the samples should promptly be transferred to tightly stoppered bottles or weighing tubes.

In technical analyses, for the purpose of determining the commercial value of an article, or of controlling processes of manufacture, materials must be analyzed as they are. But, in every case, especial care should be taken to make up a sample which will represent as nearly as possible the average composition of the whole lot.

If, on the other hand, it is desired to determine the atomic composition of a compound, it is necessary to select or prepare pure material for analysis. This may seem simpler than it really is. Many compounds absorb or give up moisture upon exposure to the air, and their treatment should vary with their nature, as illustrated in the following cases. Salts such has $Na_2SO_4 . 10 H_2O$ and $Na_2CO_3 . 10 H_2O$, which effloresce in ordinary air, may be dried, after recrystallization, by strongly pressing the powdered material between several layers of filter paper, the paper being renewed as long as moisture continues to be taken up; $MgSO_4 . 7 H_2O$ and $NaKC_4H_4O_6 . 4 H_2O$, which do not lose water of constitution in ordinary air, may be spread out upon filter paper, covered with another sheet, and allowed to dry at the ordinary temperature. Compounds such as $HFe(SO_4)_2 . 4 H_2O$ and $CaC_4H_4O_6 . H_2O$, which do not effloresce in artificially dried air, but which undergo chemical change at $100°$, may be conveniently dried in a desiccator, over calcium chloride. Substances, as $KHC_4H_4O_6$, sugar, etc., which readily give up hygroscopic moisture at $100°$, without other

alteration, are best dried in an oven at that temperature; while K_2PtCl_6, which retains moisture, or dries only slowly at 100°, but which decomposes below a red heat, should be dried in an oven at, say, 130°. Finally, substances such as NaCl, Na_2SO_4, etc. may be given a preliminary drying, in a covered vessel, at 130°, or higher, to prevent decrepitation, and then be ignited, more or less strongly, depending upon their nature. In every case, the sample should be dried, without decomposition, to constant weight.

Substances used in testing the accuracy of analytical processes, or in standardizing volumetric solutions, must also be extremely pure. In fact, compounds are generally favored which are non-hygroscopic, and which may readily be prepared in a pure condition; if possible, it is well to select compounds which normally do not contain water of crystallization. Many salts can be obtained sufficiently pure in the market; but their purity should never be accepted on faith. If tests indicate the presence of impurity, and, often, if the salt contains water of crystallization, the material should be recrystallized.

For this purpose, a convenient weight of the salt is dissolved in the least possible quantity of hot water, using a quantity of water not quite sufficient to dissolve the whole lot; the hot solution is poured into a fluted filter, held in a stemless funnel, and the filtrate is received with continuous stirring in a beaker, which itself is immersed in cold water, in a larger vessel. The rapid cooling and constant stirring cause the formation of a fine crystalline powder, which is almost free from inclosed mother-liquor. The crystalline powder is filtered off in a funnel containing a perforated platinum cone, the adhering mother-liquor being removed by suction or in a centrifuge. Two such recrystallizations will nearly always suffice. According to the nature of the substance, it is dried in the air at a specific temperature, or in a desiccator, to constant weight.

Concerning the preparation of samples for analysis by beginners in quantitative analysis, the reader should consult the appendix.

PART II

GRAVIMETRIC ANALYSIS

EXERCISES WITH THE BALANCE

Before beginning work at the balance, read carefully the rules given on pp. 9–11 of Part I, and observe them always.

Determination of the Zero-Point. Determine the zero-point of the unloaded balance, according to the method on p. 11. If the zero-point found is not more than one division from the center of the scale, the balance may be used by the student; otherwise it will be adjusted by an instructor, upon request. The beginner should not attempt this adjustment.

Determination of the Weight of an Object. Clean two porcelain crucibles, rinse them with distilled water, and allow them to drain. Place each crucible upon a pipestem triangle, supported upon a tripod, and heat with the colorless flame of a Bunsen or Tyrill burner, — gently at first, and then to a red heat. Allow the crucibles to cool off somewhat, but while still warm, place them in a desiccator, using the crucible tongs. (*After any piece of apparatus has been cleaned and ignited for weighing, it must never be handled with the fingers before the weight is taken.*) Allow the crucibles to cool in the desiccator for at least 20 minutes.

Now with the crucible tongs place a crucible on the left-hand pan of the balance, and, by means of the forceps in the weight box, place weights on the right-hand pan until they balance the crucible to within 0.005 g. Begin with a weight which you think will approximately balance the object, lower the balance beam, and gently release the pan supports. It will then be seen

which side is the heavier. Finally adjust the rider, so that, when the beam is swinging freely, the pointer traverses the same number of divisions on either side of the observed zero-point. Always try the weights in the order in which they occur in the box, beginning with the heavier weights, and using the rider for weights smaller than 5 or 10 milligrams, according to the number of large divisions on the beam.

As soon as the object appears to be balanced, raise and lower the beam, and make another observation. *Read the weight of the crucible by noting in order the vacant spaces in the box, beginning with the largest missing weight; and check this reading as the weights are returned to the box.* Be sure also to note the weight recorded by the rider, and then lift it from the beam. Always record the weight, in pencil as it is first read, and in ink after it has been checked, and always in the record book, — never on a loose sheet of paper.

In this manner, weigh the two crucibles separately, and then weigh them together, entering all three results in the notebook. (*In connection with the keeping of records, see the remarks on p. 4.*) The sum of the separate weights should agree closely with the result obtained upon weighing both crucibles together, — within, say, 0.0002 g.

THE DETERMINATION OF CHLORINE IN A SOLUBLE CHLORIDE

The sample may be pure sodium chloride, or it may be an artificially prepared mixture of sodium chloride and sodium carbonate.

Method. The aqueous solution of the chloride is acidified with nitric acid and treated with silver nitrate in excess. The chlorine is quantitatively precipitated as silver chloride, which is filtered off, washed, dried, and weighed. Other acids which yield silver salts insoluble in nitric acid must of course be absent.

A. **A Paper Filter is Used : Procedure.** Carefully clean the weighing tube containing the sample, without handling it di-

rectly with the fingers, and weigh it accurately to a tenth of a milligram. Record the weight at once in the notebook. Hold the tube over a clean 300-cc. beaker (plainly labelled " I "), remove the stopper, allowing no particles to fall from it or from the tube elsewhere than into the beaker, and carefully pour into the beaker from 0.2 to 0.3 g. of the sample. Replace the stopper in the tube, weigh accurately, and record the weight in the notebook. The difference of these two weights is the weight of the portion taken for analysis. Weigh a second portion of 0.2–0.3 g. into another beaker (labelled " II "), entering the weights and their difference in the notebook, as before.

Dissolve each portion in about 150 cc. of distilled water, and acidify the solutions with nitric acid, adding the acid slowly and with stirring, until a strip of blue litmus paper shows an acid reaction when moistened by means of the wet stirring rod with the least possible quantity of the liquid. Assuming the sample to be pure sodium chloride, calculate the volume of silver nitrate solution required in each case to effect complete precipitation (for the strength of the reagents, see the Appendix), and add slowly and with stirring about 5 cc. more than that amount. Cover the beaker with a watch glass, and heat the solution gradually to boiling, with occasional stirring. Continue the heating and stirring until the precipitate coagulates and the supernatant liquid is clear. The beaker should be kept away from direct sunlight, and the heating and stirring should be so conducted as to avoid any possibility of loss. Finally, add to the clear liquid a drop or two of silver nitrate solution, to test for complete precipitation; if a precipitate forms, add 5 cc. more, and test again.

Prepare two ashless filters (9 cm. in diameter), according to the directions given on p. 30, and decant the hot liquid through the filter in each case, leaving the precipitate as far as possible in the beaker. Unless the filtrates are perfectly clear and free from particles of silver chloride, they must be refiltered through the same filters. If they are perfectly clear, and the tests show

complete precipitation, pour them into one of the laboratory receptacles for " Silver Residues," wash the beakers with tap water and then with distilled water, and replace them under the funnels. Now wash the precipitates twice by decantation with 10 cc. portions of hot water, acidified with a drop or two of nitric acid, pouring the washings through the filters, and finally transfer each precipitate to the corresponding filter by means of a stream of hot water from the wash bottle, loosening the adhering particles with the aid of a " policeman " (see p. 32). Wash the filters and precipitates with hot water until 3 cc. of the washings show no cloudiness or opalescence with *one drop* of dilute hydrochloric acid. After allowing the filters to drain, cover each funnel with an *ordinary* filter paper, crimping the edges of the paper over the sides of the funnel. The funnels, properly numbered, and labeled with the student's name and desk number, should then be placed in a drying oven, at a temperature of 90°–100°, and left there *until completely dry*.

Now, in the case of each precipitate, open the filter over a piece of smooth glazed paper, about six inches in diameter, and, by finally rubbing the sides of the filter gently together, transfer the precipitate as completely as possible to the center of the glazed paper. Be careful not to rub off any appreciable quantity of the paper, nor to lose any of the silver chloride in the form of dust. Cover the precipitate on the paper with an inverted funnel or watch glass, to protect it from dust and air currents.

Carefully refold the paper, flat, bend the top over, and roll the paper into a small bundle; then place it in a weighed porcelain crucible. Place the crucible upon a triangle, incline it about 45°, and ignite gently until the volatile products are expelled from the paper. Then, with the flame well at the base of the inclined crucible, ignite strongly until all the carbon is consumed. (See Part I, p. 38.) Allow the crucible to cool, add two drops of 6-normal nitric acid and one of hydrochloric acid, and heat *with the greatest caution*, to avoid spattering, until the acids are expelled. Transfer the bulk of the precipitate quantitatively from

the glazed paper to the cooled crucible, placing the latter on a second piece of glazed paper and brushing the precipitate into it, with a small camel's hair brush.

Moisten the precipitate with two drops of nitric, and one drop of hydrochloric acid, carefully expel the acids, and then *gradually* raise the temperature until the salt *just begins* to fuse. Allow the crucible to cool in a desiccator, and weigh it. Repeat the heating, without the addition of acids, and weigh the cooled crucible. The heating and weighing must be repeated until the weight is constant within 0.2 mg. after two consecutive heatings. From the weight of silver chloride obtained in each case, calculate the percentage of chlorine in the sample.

Finally, place the ignited precipitates in one of the laboratory receptacles for silver residues. The chloride which adheres to the crucible may be loosened by covering it with dilute sulphuric acid and adding a small quantity of granulated zinc.

NOTES. — 1. The solution is acidified with nitric acid, before precipitation with silver nitrate, to prevent the precipitation of substances such as silver oxide, carbonate, phosphate, etc., which are insoluble in water but soluble in nitric acid. The acid also helps to coagulate the precipitate. A large excess of the acid is to be avoided, since it would slightly increase the solubility of the precipitate.

2. It is safer not to boil the acidified solution until after silver nitrate has been added in excess, since otherwise a slight amount of chlorine might be set free by the nitric acid and lost by volatilization. The presence of an excess of silver nitrate can easily be recognized at the time of its addition, by the increased readiness with which the precipitate coagulates and settles.

3. The precipitate should not be exposed to strong sunlight, since by its action a slight amount of chlorine is set free. The superficial alteration which the chloride undergoes in diffused daylight may readily be counteracted by the treatment with nitric and hydrochloric acids; but the loss in weight due to this cause is really too insignificant to affect the accuracy of the determination.

4. The precipitate and filter are washed with water to remove the non-volatile nitrates of silver and sodium, as well as any other soluble impurities. It may be assumed that these are all removed as soon as 3 cc. of the washings give no cloudiness with a drop of hydrochloric acid. Only a single drop should be added, because silver chloride is somewhat soluble in this

acid. The wash water should be hot in order to prevent the precipitate from going into colloidal solution; it is still safer to acidify the water slightly with nitric acid.

5. The bulk of the precipitate must be separated from the filter, because the burning organic matter would reduce a considerable quantity of the precipitate to metallic silver, and its complete reconversion to the chloride within the crucible, by means of acids, would be uncertain. The small quantity which adheres to the filter, and which is more or less completely reduced during ignition, is easily reconverted to chloride by the treatment with nitric and hydrochloric acids.

6. Silver chloride should not be heated to complete fusion, since a slight loss by volatilization might take place. The temperature of fusion is sufficient to completely remove adsorbed water and acids, but it is not always sufficient to destroy filter shreds. Although these would probably be completely oxidized by the nitro-hydrochloric acid and subsequent ignition, they should not be allowed to contaminate the precipitate.

7. The ignited precipitate of silver chloride, as well as the filtrates which contain an excess of silver nitrate, should be placed in the receptacles for silver residues; the silver can easily be recovered.

Assuming that, on the average, duplicate determinations require 55 cc. of 0.2-normal silver nitrate solution, the residues returned in the case of each student should contain about 1.2 g. of metallic silver. Taking into account the number of analyses which have to be repeated, a class of one hundred students will usually return in residues at least 150 g. (about 5 oz.) of metallic silver.

8. Silver chloride is almost insoluble in water. The solubility varies somewhat with its physical condition, and is about 1.12 mg. per liter at 20° C. Owing to the common-ion effect, the solubility is still less in a very dilute solution of silver nitrate or of hydrochloric acid. In hot water the salt is more soluble, 21.8 mg. per liter at 100° C.; but, fortunately, the speed of solution is so slow that the precipitate may be thoroughly washed with hot water, without undue error from this cause.

Silver ion has a great tendency to enter into the formation of complex ions, as $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[AgS_2O_3]^-$, etc., and the chloride is therefore readily soluble in aqueous ammonia, in alkali cyanide solutions, and in sodium thiosulphate ("hypo") solution. Silver chloride is also soluble in strong hydrochloric acid and in other chloride solutions, probably with the formation of a complex anion, such as $[AgCl_2]^-$; it is also soluble in concentrated silver nitrate solution, and in strong nitric acid. When boiled with concentrated sulphuric acid, it is converted into silver sulphate, and by zinc and dilute sulphuric acid it is reduced to metallic silver.

B. **A Gooch Crucible is Used: Procedure.** Weigh out two samples of the substance, of about 0.25 g. each, and convert the chloride into silver chloride as described in procedure *A*. Meanwhile, prepare two Gooch crucibles, following the directions on pp. 33–35; and finish the analysis according to the details there given.

NOTE. — Bromides, iodides, cyanides, sulphocyanates, etc., as well as silver itself, may be determined in a similar manner, with the use of Gooch crucibles. Chlorates, etc., may be determined by first reducing them to chlorides, and then precipitating with silver nitrate.

For the determination of these substances when two or more of them are present in the same sample, the student is referred to the larger works on quantitative analysis. (But see also Part IV, Problems 37, 38, 90, 91, and 93.)

THE DETERMINATION OF IRON AND OF SULPHUR IN A SOLUBLE SULPHATE OF IRON

The sample may be pure ferrous ammonium sulphate, pure ferric alum, or an artificially prepared mixture of anhydrous ferric sulphate, sodium carbonate, and potassium sulphate. This mixture is readily soluble in dilute hydrochloric acid.

Method. The sample is dissolved in water, with the addition of hydrochloric acid, after which the iron is oxidized to the ferric condition, unless it is already wholly present in that state. The iron is then separated, by double precipitation with ammonium hydroxide, as ferric hydroxide. The precipitate is ignited, and weighed as ferric oxide.

From the combined filtrates and washings, which must have a large volume, and which must be free from nitrates, etc., the sulphate is precipitated by means of a dilute solution of barium chloride. The precipitate is ignited, and weighed as barium sulphate.

A. **Procedure for the Determination of Iron.** Weigh out into dry 200 cc. beakers two portions of about one gram each, and add to each portion 50 cc. of water and 10 cc. of 6-normal hydrochloric acid, keeping the beakers covered with watch-

glasses to prevent loss by effervescence. Treat each solution as follows: Heat to boiling, and add, drop by drop, nitric acid (sp. gr., 1.42),[1] until the brown coloration at first imparted to the liquid gives place to a yellow or red. (Note the volume of nitric acid which is added; 1 cc. will always be found sufficient.) Boil for three minutes, and pour the solution, with stirring, into an excess of ammonia which has been diluted with water to a volume of 200 cc. (For this purpose, calculate the volume of 6-normal ammonium hydroxide required to neutralize the acids added, and use 5 cc. in addition.) Heat the mixture to boiling, and allow the precipitate to settle. Decant the boiling-hot, clear liquid through an ashless filter (9 cm. in diameter), leaving the precipitate as far as possible in the beaker, and wash twice by decantation with 50 cc. portions of very hot water, still leaving the precipitate in the beaker. (At once neutralize the filtrate and washings with hydrochloric acid, and reserve for the sulphate determination. *Their evaporation, as directed under the determination of sulphur, should be begun at this point.* See p. 4.)

Dissolve the precipitate by pouring through the filter a boiling mixture of 5 cc. of water and 10 cc. of 6-normal hydrochloric acid, adding the acid in small portions, and collecting the filtrate (and washings) in the beaker containing the bulk of the precipitate, which also should completely dissolve. After thoroughly washing the filter, tear it into small bits and add these to the ferric chloride solution. Pour this mixture into an excess of ammonia, as before, and heat to boiling. Filter boiling-hot through a fresh filter, wash the precipitate twice by decantation with hot water, and finally transfer it to the filter; wash continuously with hot water until 3 cc. of the washings show no turbidity when treated with a drop of nitric acid and one of silver nitrate solution. (The combined filtrate and washings should at once be neutralized with hydrochloric acid and added to those from the first precipitation; the evaporation should be allowed to continue.)

Ignite the precipitate, together with the filter, in an inclined

[1] Before adding nitric acid, see Note 2.

platinum or porcelain crucible. After the volatile matter of the filter has been expelled, raise the temperature to the full heat of the burner, and, with the flame well at the base of the inclined crucible, continue the heating for about 15 minutes. Cool in the desiccator, and weigh. Repeat the heating until the weight is constant within 0.2 mg. Report the percentage of iron in the sample.

NOTES. — 1. In ferrous salt solutions the iron is slowly oxidized by oxygen from the air ($4 Fe^{++}+O_2+2 H_2O=4 Fe^{+++}+4 OH^-$), and, unless the solution contains free acid to remove the OH^- ions, the iron will partially precipitate in the form of a basic ferric sulphate. Moreover, owing to hydrolysis, upon boiling an aqueous solution of ferric sulphate there results a partial precipitation of the iron, again in the form of a basic ferric sulphate (*e.g.* $Fe_2(SO_4)_3+2 H_2O=2 Fe(OH)SO_4+H_2SO_4$). This action, however, is prevented by the presence of sufficient hydrochloric acid.

2. The complete oxidation of the iron is necessary, since ferrous iron is not quantitatively precipitated by ammonia. In the absence of air, indeed, ammonium salts are capable of preventing entirely the precipitation of iron from ferrous salt solutions. Ferric iron, in the absence of organic matter, is completely precipitated by ammonia, even in the presence of ammonium salts.

The nitric acid oxidizes the iron according to the equation: $6 FeSO_4+2 HNO_3+6 HCl=2 Fe_2(SO_4)_3+2 FeCl_3+2 NO+4 H_2O$, and the dark color imparted to the solution is due to the union of the nitric oxide with ferrous salt which has not yet been oxidized, to form an unstable nitroso-compound similar to that formed in the "ring-test" for nitrates. The nitric oxide is expelled by heat, and the solution finally acquires the yellow color which is characteristic of ferric chloride in the presence of hydrochloric acid.

To insure the presence of iron wholly in the ferric condition, a very small quantity of the oxidized solution should be tested on a porcelain plate with a drop of very dilute, freshly prepared potassium ferricyanide solution (a piece of the salt the size of a pinhead, in 20 cc. of water). If the solution has a volume of 50 cc., and an ordinary drop a volume of 0.05 cc., then the loss of the latter would occasion an experimental error of 0.1% in the iron (and in the sulphur) determination. In this case, therefore, we might add a couple of drops of the solution to 1 cc. of water in a clean watch glass, and use one drop of this mixture for the test; the remainder can then be washed back into the beaker containing the bulk of the solution. The error is thus reduced to 0.01%, which is negligible.

Much time can often be saved by testing in this way the solution made from a very small portion of the (unweighed) original sample, for ferrous iron; *in its absence the addition of the nitric acid, and the subsequent evaporation to dryness, should be omitted.*

3. If ammonia is added to ferric sulphate solution, the ferric hydroxide precipitate is apt to be contaminated with sulphuric acid, in the form of a basic ferric sulphate. A gradual neutralization with ammonia is almost sure to lead to the separation of an insoluble basic sulphate, owing to a deficiency of hydroxide ions. If, however, the iron solution is added with stirring to an excess of aqueous ammonia, the precipitate obtained will be comparatively free from basic sulphate. But, since even here the basic salt is likely to be present in small quantity, the precipitate is redissolved and the solution again added to an excess of dilute ammonia.

4. To avoid errors due to the solvent action of ammonium hydroxide upon glass, the precipitate should be filtered off without unnecessary delay. It is for this reason, also, that the filtrates and washings should be promptly neutralized with hydrochloric acid. The ferric hydroxide precipitate should under no circumstances be allowed to dry before the washing has been completed; it would be sure to crack, and in a subsequent washing the wash water would simply run through the crevices.

5. During the combustion of the filter, a portion of the precipitate may be reduced to Fe_3O_4, and it is essential that any of this substance should be oxidized back to ferric oxide. Therefore, during the ignition, it is important that there should be a ready access of air to the precipitate. For this reason it is directed to macerate the filter with the solution of ferric chloride before the second precipitation; this insures a very porous mass which is readily reoxidized.

6. The foregoing method may be used for the gravimetric determination of aluminum or chromium, with the additional precaution that the solution, before it is filtered, must be heated until but a very slight excess of ammonia remains, the hydroxides of these metals being more soluble in aqueous ammonia than ferric hydroxide.

If it is desired by this method to determine the chromium in an alkali chromate, the latter is boiled with hydrochloric acid and alcohol, in order to reduce the chromium to the trivalent condition.

$$(K_2Cr_2O_7 + 3\ C_2H_6O + 8\ HCl = 2\ KCl + 2\ CrCl_3 + 3\ C_2H_4O + 7\ H_2O).$$
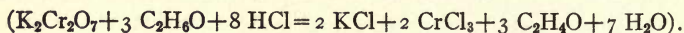
The hydroxides of all three metals are precipitated by sodium or potassium hydroxide, but the precipitates are always contaminated with alkali. Furthermore, aluminum and chromium hydroxides dissolve readily in an excess of caustic alkali and form anions, to which the formulas AlO_2^- and CrO_2^- are usually ascribed. When freshly precipitated, all three hydroxides

dissolve in hydrochloric acid; but aluminum hydroxide, after standing for some time, dissolves with considerable difficulty. While their precipitation is favored by the presence of ammonium salts (coagulation), it is entirely prevented by the presence of sufficient tartaric acid (formation of soluble complexes); citric acid, glycerol, sugars, etc. resemble tartaric acid in this respect.

Upon ignition, each hydroxide yields an oxide suitable for weighing — Fe_2O_3, Al_2O_3, Cr_2O_3. Chromic oxide, however, upon ignition, is partially oxidized to $Cr_2(CrO_4)_3$; it should be ignited in a current of hydrogen (G. Rothaug, *Zeitschrift für anorganische Chemie*, Vol. 84, pp. 165–189 (1913)).

B. **Procedure for the Determination of Sulphur.** Evaporate to dryness, on the steam bath, the combined filtrates and washings from the iron determination; add to the residue 10 cc. of 6-normal hydrochloric acid; and again evaporate to dryness.[1] Dissolve the residue in 100 cc. of water, and filter the solution if it is not perfectly clear. Transfer the solution to a 700 cc. beaker, dilute to 400 cc., and then add 1.5 cc. of 6-normal hydrochloric acid. Heat the solution to boiling, and, with stirring, quickly pour in a boiling mixture of 15 cc. of 1-normal barium chloride solution and 100 cc. of water. Continue the boiling and stirring for two or three minutes; allow the precipitate to settle, and, at the end of half an hour, after testing for complete precipitation, decant the liquid through a filter. Substitute a clean beaker for the beaker containing the clear filtrate, wash the precipitate by decantation with hot water, and subsequently upon the filter with hot water until 3 cc. of the washings give no cloudiness or opalescence with a drop of silver nitrate solution and one of nitric acid. The precipitate is then dried and ignited to constant weight, with the flame well at the base of the inclined crucible. Report the percentage of SO_4 in the sample.

NOTES. — 1. Barium sulphate, to a greater degree than most precipitates, tends to carry down other salts which are present in the solution from which it separates, and these substances cannot be removed by simply washing the precipitate. This is especially true of nitrates and chlorates,

[1] In case the original sample contained no ferrous iron, and the addition of nitric acid was omitted, it is sufficient only to evaporate the neutralized filtrates and washings to about 300 cc. This liquid is then transferred to the beaker, diluted to about 400 cc., and treated further as described in the procedure.

and of the salts of trivalent metals, such as iron, chromium, etc. Therefore, if nitric acid has been used to oxidize the iron, it must be completely removed by evaporation with a large excess of hydrochloric acid.

Iron is always present in the sulphate precipitated from hot solutions in the presence of ferric salts, and the precipitate then loses sulphuric acid upon ignition, and gives low results in spite of its iron content. Pure barium sulphate itself is not decomposed at a red heat, but suffers loss, probably of sulphur trioxide, at a temperature above 900°.

Barium sulphate requires about 400,000 parts of water for its solution, but it is more soluble in hydrochloric acid, even very dilute. In many salt solutions it is still more soluble than in water acidified with hydrochloric acid.

2. In the precipitation of sulphuric acid with barium chloride, the solution should contain only salts of the alkali metals and ammonium, and it should be free from nitrates and chlorates. Even alkali salts and barium chloride are carried down to some extent by barium sulphate, more or less in proportion to their concentration, and consequently the solution should be dilute. Since, further, the solubility of barium sulphate, as well as the amount of barium chloride carried down, increases with the concentration of the hydrochloric acid present, the quantity of the latter should be reduced to a minimum; some, however, must be present, since otherwise the precipitate would be very fine grained, and therefore difficult to filter.

Barium sulphate carries down quantities of chlorine varying from traces to as much as 1%, depending upon the conditions, and these should therefore be very carefully regulated. For a quantity of sulphate corresponding to 1–2 g. of $BaSO_4$, the latter should be precipitated from a solution which has been diluted to about 400 cc., and which should contain 1.5 cc. of free 6-normal hydrochloric acid. This solution should be boiling hot, and, for each gram of barium sulphate, 10 cc. of 1-normal barium chloride solution diluted to 100 cc., and boiling hot, should be poured in, all at once, with constant stirring. In this way exact results can be obtained, but only owing to a compensation of errors: although a very small quantity of barium sulphate remains dissolved in the acidified salt solution, an approximately equal weight of barium chloride is contained in the ignited precipitate.

3. Owing to the tendency of the precipitate to pass through the pores of the filter, the filtrate and washings should always be carefully examined for minute quantities of the sulphate. This is best accomplished by imparting to the liquid a gentle rotary motion, so that, if present, the sulphate will collect at the center of the beaker.

4. A partial reduction of barium sulphate to sulphide may be caused by the action of the burning carbon of the filter; in order to prevent the reduction of any considerable quantity, the crucible should not be heated

above dull redness until after the carbon has been consumed. Subsequent ignition, with ready access of air, will then suffice to reconvert the sulphide to sulphate. If considerable sulphate is reduced, it may be necessary to moisten the precipitate with sulphuric acid, and then to heat cautiously until the excess of acid is expelled.

THE DETERMINATION OF SULPHUR IN ORES

Method. The ore is heated with strong nitric acid and potassium chlorate, which oxidize the sulphur to sulphuric acid. After removing the nitric acid and chlorate, as well as the iron, lead, etc., the sulphuric acid is precipitated with barium chloride, and weighed as barium sulphate.

Procedure. Treat 0.25–0.50 g. samples of the finely pulverized ore (depending upon the sulphur content) in 250 cc. Erlenmeyer flasks with 10 cc. of nitric acid (sp. gr. 1.42), and heat very gently until the red fumes have somewhat abated. Then increase the heat, and add to the quietly boiling liquid potassium chlorate, from time to time, in 0.1 g. portions, until any free sulphur which has separated is entirely oxidized and dissolved; finally add 0.5 g. of solid sodium chloride and evaporate the solution to dryness. After cooling, cautiously add 10 cc. of hydrochloric acid (sp. gr. 1.19), heat gently until solution is as complete as possible, and evaporate to dryness. Take up in 5 cc. of strong hydrochloric acid, heat to boiling, and dilute with 100 cc. of cold water. To the *cold* solution add three drops of methyl orange, and ammonia to alkaline reaction; then add 5 cc. more of ammonia and 10 cc. of ammonium carbonate solution. Heat to boiling, allow the precipitate to settle in the hot liquid, and filter while still hot, washing thoroughly with hot water, and receiving the filtrate and washings in a 700-cc. beaker. Neutralize the filtrate with hydrochloric acid, and add 1.5 cc. of the 6-normal acid in excess. Dilute the solution to 400 cc., heat to boiling, and add with stirring a boiling-hot mixture of 10 cc. of 1-normal barium chloride solution and 100 cc. of water. Allow the mixture to stand for half an hour, test for complete pre-

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cipitation, and finish the determination as described in the previous Procedure.   Report the percentage of sulphur in the sample.

NOTES. — 1. Barium sulphate, if present in the ore, remains practically unaffected by the above acid treatment.   If it is desired to determine the total sulphur in ores containing barium, the hydrochloric acid solution, after the removal of nitrates and chlorates and dilution with 100 cc. of water, may be treated with 5 g. of solid ammonium chloride (to hold any lead in solution), heated to boiling, and filtered from the insoluble residue. The filter containing the latter is destroyed by ignition in a platinum crucible, and the residue fused with an excess of sodium carbonate.   The fusion is extracted with hot water and the residue washed with sodium carbonate solution; the filtrate and washings, which contain sodium sulphate, are added to the hydrochloric acid filtrate containing the bulk of the sulphur. The united filtrates are then treated with ammonia and ammonium carbonate, as described above.

2. The small amount of sodium chloride is added before the first evaporation in order to prevent the possible loss of any free sulphuric acid which might be present, — as, for example, in the analysis of pyrites.   The potassium chlorate added would, however, probably be sufficient in most cases to accomplish this result.   In the analysis of pyrites, which contains a very high percentage of sulphur, samples should be used of only 0.25 g. Otherwise the procedure is the same.

3. Upon adding ammonia in excess to the solution and heating to boiling, there is practically no danger of losing sulphur in the form of basic ferric sulphate.   (In this connection see Note 3 of the foregoing Procedure.)   The ammonium carbonate is added in order to remove any lead which may be present, as the carbonate, and thus prevent the loss of sulphur, as $PbSO_4$, before the precipitation with barium chloride.

4. In neutralizing a solution with the use of methyl orange, the solution should be cold, since otherwise the methyl orange is not a satisfactory indicator.

5. The student should be sure to read the notes on the determination of sulphur in iron sulphate, and also Problems *vi*, 12 and 13, of Part IV.

THE DETERMINATION OF PHOSPHORIC ANHYDRIDE IN PHOSPHATE ROCK

Method.   The finely ground mineral is heated with nitric acid, the mixture evaporated to dryness, and the residue extracted with hot nitric acid; the solution is then filtered from

the insoluble silicious material. The filtrate is made almost neutral with ammonia, and is treated with a solution of ammonium molybdate, in excess, to separate the phosphoric acid from calcium, iron, aluminum, etc. The precipitated ammonium phospho-molybdate is washed with acidified ammonium nitrate solution, dissolved in ammonium hydroxide, and the phosphoric acid precipitated with magnesia mixture. The magnesium ammonium phosphate is finally ignited to magnesium pyrophosphate, which is weighed.

Procedure. Weigh out two portions of the finely ground mineral, not to exceed 0.2 g. each, into 200-cc. beakers, and treat each as follows. Pour over the sample 20 cc. of 6-normal nitric acid and warm gently until solvent action has ceased; then evaporate the mixture to dryness on the steam bath. Allow the dry residue to remain for half an hour on the steam bath, and then heat it again for a few moments with 20 cc. of the nitric acid. Filter off any siliceous residue and wash several times with *small* portions of hot water, receiving the filtrate and washings in a 400-cc. beaker. Finally test the washings with ammonia for calcium phosphate, but add to the original filtrate all such test solutions in which a precipitate appears. Cautiously, and with stirring, add ammonia to the filtrate and washings until the precipitate just fails to redissolve, then nitric acid, drop by drop, until the cloudiness disappears. The volume of the liquid at this point should not exceed 100 cc.

Heat the solution until it cannot be held comfortably in the hand, remove the burner, and add 75 cc. of a freshly filtered solution of ammonium molybdate which has been gently warmed. Digest for an hour at 60–65°, and then decant the supernatant liquid through a filter; wash the yellow precipitate by decantation with acid ammonium nitrate solution [1] (still keeping the bulk of the precipitate in the beaker), until 3 cc. of the washings give no test for calcium with ammonia and ammonium oxalate.

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[1] Made by mixing 50 cc. of 6-normal ammonium hydroxide with 100 cc. of 6-normal nitric acid, and diluting the mixture with 350 cc. of water.

The filtrate should not be thrown away, but should be tested for complete precipitation by renewed digestion with 5 cc. of moybdate reagent; it should then be placed in a receptacle for " Molybdate Residues."

Dissolve the ammonium phospho-molybdate by pouring over the filter four separate 10 cc. portions of a warm 2.5 per cent solution of ammonia [1] (afterwards washing the filter five times with 10 cc. portions of hot water), and receiving the filtrate and washings in the beaker containing the bulk of the precipitate. To the clear solution add hydrochloric acid, drop by drop, with stirring, until the yellow cloudiness produced disappears only slowly upon stirring. To this solution add 20 cc. of magnesia mixture from a pipette, at the rate of about 1 drop per second, with vigorous stirring (see Note 7; the last 10 cc. may be added somewhat faster). Let stand for 15 minutes, add 15 cc. of ammonia (sp. gr., 0.90), and then, after a period of 2 or 3 hours, decant the clear liquid through a filter and transfer the precipitate to the filter by means of 2.5 per cent ammonia water. Continue the washing with this liquid until 3 cc. of the washings, after acidification with nitric acid, give no opalescence with silver nitrate solution. Finally test the filtrate for complete precipitation.

Dry the filter in the covered funnel, and then ignite, being careful to raise the temperature slowly and to insure the presence of plenty of air. Do not raise the temperature above moderate redness until the precipitate is white. Finally ignite to constant weight at the blast lamp, over a large Meker burner, or, preferably, in an electric furnace. Report the percentage of P_2O_5 in the sample.

Notes. — 1. The dehydration and removal of any dissolved silicic acid is necessary, since otherwise it would tend to partially separate with the phospho-molybdate precipitate, and render the latter more or less insoluble in ammonia.

[1] Made by mixing 10 cc. of 6-normal ammonium hydroxide with 30 cc. of hot water.

When washing the siliceous residue the filtrate may be tested for calcium by simply adding ammonia, which neutralizes the acid holding calcium phosphate in solution and causes precipitation.

2. Nitric acid is used as the solvent because the phospho-molybdate is somewhat soluble in hydrochloric acid. Nitric acid exerts a slight solvent action, but this is counteracted by the presence of ammonium nitrate; hence the partial neutralization of the nitric acid with ammonia, and the washing with nitric acid containing an equivalent of ammonium nitrate.

It should be noted that the molybdate reagent contains ammonium nitrate and free nitric acid. (See the Preparation of Reagents, in the Appendix.)

3. The precipitation of the phosphoric acid as magnesium ammonium phosphate from the original solution of the rock is not possible, owing to the presence of metals such as iron, aluminum, calcium, etc., which form phosphates insoluble in ammonia. For that reason the phosphoric acid is first separated from the metals, in the presence of nitric acid, by means of ammonium molybdate.

4. While the composition of the yellow precipitate varies somewhat with the conditions, it nevertheless seems to correspond pretty closely to the formula $(NH_4)_3PO_4 . 12 MoO_3 . 2 HNO_3 . H_2O$; at any rate, the ratio $P_2O_5 : 24 MoO_3$ holds good. The yellow precipitate dissolves in ammonia to give ammonium phosphate and ammonium molybdate, and molybdic acid is not precipitated by magnesia mixture.

5. The precipitation of the phospho-molybdate is more prompt in warm than in cold solutions, but the temperature should not exceed 65°; at higher temperatures molybdic acid, which is white, tends to separate. Vigorous stirring also promotes the separation of the yellow precipitate.

A large excess of the molybdate reagent is required to effect a complete precipitation of the phosphoric acid. Theoretically 1.95 g. of MoO_3 are required to combine with the phosphorus in 0.2 g. of rock containing 40 per cent of P_2O_5; while the quantity of the reagent actually used (75 cc.) contains about 5 g. of MoO_3. The presence of ammonium nitrate in the solution is also conducive to complete precipitation. These substances, by mass action, prevent the partial dissociation of the complex into its more soluble constituents.

6. If magnesium ammonium phosphate is washed with pure water, it is hydrolyzed according to the equation,

$$MgNH_4PO_4 + H_2O \rightleftharpoons MgHPO_4 + NH_4OH.$$
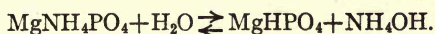
It thereby loses its crystalline form, and is almost sure to give a cloudy filtrate. In the presence of ammonium hydroxide, however, this decomposition is prevented by mass action.

7. The precipitate of magnesium ammonium phosphate should be perfectly crystalline; the slow addition of the reagent, with constant stirring, is essential to this end, but the stirring rod should not be allowed to scratch the beaker.

A large excess of magnesia mixture tends to cause the precipitate to carry down molybdic acid, as well as magnesia (shown by a persistently flocculent precipitate). In such cases the precipitate should be redissolved by adding a small quantity of hydrochloric acid, the solution treated with 2 cc. of magnesia mixture, and the hot liquid slowly neutralized with 2.5 per cent ammonia. Strong ammonia is then added, and the analysis continued as above.

"Magnesia Mixture" is prepared by putting together in solution magnesium chloride, ammonium chloride, and ammonium hydroxide. The function of the ammonium chloride is to prevent the precipitation of magnesium hydroxide, so that the composition of the precipitate may correspond to the formula, $MgNH_4PO_4 . 6 H_2O$.

8. Upon ignition, the magnesium ammonium phosphate gives off ammonia and water, and is converted into magnesium pyrophosphate: $2 NH_4MgPO_4 . 6 H_2O = Mg_2P_2O_7 + 2 NH_3 + 13 H_2O$. The precautions detailed in Part I should be observed with great care during the ignition of this precipitate. There is danger here of a partial reduction of the phosphate by the ammonia or by the carbon of the filter, and also, if too soon heated very strongly, the precipitate becomes glazed over and it is then practically impossible to remove the carbon by further heating. The precipitate is much more readily ignited to whiteness in platinum than in porcelain; but in case platinum is used, especial care should be taken to provide a plentiful supply of air. Reduction of the phosphorus would play havoc with the crucible.

The most satisfactory procedure is to filter off the magnesium ammonium phosphate in a Munroe crucible of platinum (with a platinum sponge filter), in which the precipitate can be ignited without danger of loss. If a good muffle furnace (preferably electric) is available, a Gooch crucible of porcelain may be used with advantage.

THE DETERMINATION OF CALCIUM AND MAGNESIUM OXIDES IN LIMESTONE

Method. The hydrochloric acid extract of the limestone[1] is freed from dissolved silica, treated with bromine water and ammonia, to remove iron, aluminum, manganese, etc., and from

[1] See Note 1.

the filtrate the calcium is precipitated with ammonium oxalate, the precipitate being ignited to the oxide. The filtrate from the calcium oxalate is treated with sodium phosphate and ammonia, the precipitate of magnesium ammonium phosphate being ignited to magnesium pyro-phosphate.

A. **Procedure for the Determination of Calcium.** Weigh out into two casseroles 0.5–0.6 g. samples of the finely ground rock, and treat each as follows: Cautiously moisten the powder with 5 cc. of water, cover the casserole, add 10 cc. of 6-normal hydrochloric acid in small portions, and evaporate to dryness on the steam bath. Pour over the residue 5 cc. of water and 10 cc. of the hydrochloric acid, evaporate to dryness, and heat the dry residue for half an hour on the steam bath. Pour over this residue 5 cc. of water and 10 cc. of the 6-normal acid, and heat gently for 10 minutes; filter and wash twice with 5 cc. portions of dilute hydrochloric acid, and finally with water until free from chlorides. (See Note 1 in regard to the insoluble residue.)

Add to the filtrate and washings enough bromine water to impart a distinctly yellow tinge, boil, and then add ammonia until its odor persists in the solution. Heat until the excess of ammonia is largely expelled, and filter promptly. Wash the filter twice with hot water, allowing the washings to run into the beaker containing the filtrate. Now pour through the filter 25 cc. of hot hydrochloric acid (one volume of the 6-normal acid to 5 of water), and if there is a brown insoluble residue allow it to remain on the filter; the acid solution should be received in the beaker in which the ammonium hydroxide precipitate was obtained. Wash the filter five times with hot water, and then reprecipitate the iron, etc., from the filtrate and washings with bromine water and ammonia as already described. Collect the precipitate on the filter already used, and wash it free from chlorides with hot water; add the filtrate and washings to those at first obtained. (Concerning the precipitate, see Note 1.)

Evaporate the combined filtrates and washings to a volume of about 200 cc. Heat the solution to boiling; if necessary, add

ammonia until its odor is plainly perceptible; and then add ammonium oxalate solution slowly and with stirring, in moderate excess. Boil for two minutes, allow the precipitate to settle for half an hour, and decant through a filter into a beaker, washing the precipitate twice with hot water containing a few cubic centimeters of ammonium oxalate solution and a very little ammonia. Test the filtrate with ammonium oxalate for complete precipitation, and if no precipitate forms in 15 minutes, acidify the solution with hydrochloric acid and reserve it for the magnesium determination.

Redissolve the calcium oxalate with warm hydrochloric acid (one volume of the 6-normal acid to one of water), pouring the acid through the filter and receiving it in the beaker containing the bulk of the precipitate. Wash the filter three times with water, and twice with very dilute ammonia. Dilute the solution to 250 cc., heat to boiling, add 1 cc. of ammonium oxalate solution, and ammonia in slight excess; boil for two minutes, and set aside for half an hour. Filter off the precipitate upon the filter previously used, and wash it free from chlorides with hot water containing a few drops of ammonium oxalate solution and a very little ammonia. (The filtrate and washings should at once be acidified with hydrochloric acid and combined with those from the first precipitation. If not already started, the evaporation of these filtrates should be begun at this point.)

Gently ignite the dried precipitate and filter until the latter is consumed, and then heat with the full flame of the burner for 45 minutes; finally heat for three minutes over the blast lamp. Repeat the heating at the blast lamp, until the weight becomes constant. (A muffle furnace is preferable for the ignition, after the filter is consumed.) Report the percentage of CaO found.

NOTES. — 1. The chief component of limestone, calcium carbonate, is readily attacked by hydrochloric acid, as also are some of the other components; but few limestones are so pure as to dissolve completely in hydrochloric acid. The residue may contain quartz, silicates, pyrites, or other refractory materials, and carbonaceous matter may also be present.

Furthermore, the insoluble silicates of the residue are apt to contain some calcium and magnesium. The thorough analysis of a limestone necessitates the use of an elaborate system of procedures and the determination of numerous substances, but for many technical purposes the analysis may be confined to the determination of the insoluble matter and silica, of the oxides of iron and aluminum (including small quantities of the oxides of titanium, manganese, phosphorus, etc.), of calcium oxide, and of magnesium oxide.

In this exercise, the insoluble residue, if ignited and weighed, would give a more or less accurate approximation of the insoluble matter and silica, and the ignited ammonium hydroxide precipitate would roughly approximate the summation of the oxides of iron, aluminum, titanium, etc., *in the soluble portion*. It should be remembered, however, that substances such as hydrous silicates, pyrites, and carbonaceous matter in the insoluble residue, and ferrous and manganous oxides (originally present as carbonates) in the soluble portion, would not be correctly indicated by this method.

It should be noted that the amount of insoluble residue and also its character will often depend upon the concentration of the acid used for the solution of the limestone, and that the determination of this residue is essentially empirical.

For a description of the complete analysis of limestones, the student should refer to Bulletin 422 of the United States Geological Survey, by W. F. Hillebrand.

2. Some of the silicates present are apt to be at least partly decomposed by the acid, and the soluble silicic acid must be dehydrated and rendered insoluble by evaporation and heating. The residue is washed first with dilute acid to prevent the separation on the filter of basic salts of iron, aluminum, etc., owing to the hydrolytic action of water.
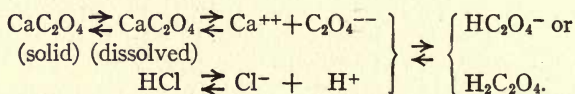
3. The addition of bromine water serves to oxidize any ferrous iron, and also manganese, which precipitates as $MnO(OH)_2$. The ammonium hydroxide precipitate should be filtered off promptly, since the alkaline solution absorbs carbon dioxide from the air, with the consequent precipitation of a little calcium as the carbonate. This is always possible, and for that reason, as well as because the precipitated hydroxides also tend to carry down the hydroxides of calcium and magnesium, the precipitate is redissolved and again precipitated, to free it from these metals.

4. The accurate separation of calcium and magnesium by means of ammonium oxalate requires considerable care. The calcium oxalate tends to carry down some magnesium oxalate, probably in the form of a double salt, but this can be removed by dissolving the precipitate and reprecipitating the calcium in the presence of only this small amount of magnesium.

If the proportion of magnesium is not very large, the calcium can be separated by precipitation from a rather dilute solution, with the addition of more than enough ammonium oxalate to convert both the magnesium and calcium into oxalates. (In this connection, see T. W. Richards, C. T. McCaffrey, and H. Bisbee; *Zeitschrift für anorganische Chemie*, **28**, p. 71 (1901).)

5. The small quantity of ammonium oxalate solution is added before the second precipitation of the calcium, because an excess of the reagent reduces the solubility of the calcium oxalate, and also tends to hold the magnesium in solution in the form of a double magnesium ammonium oxalate. For the first reason, the precipitate is washed, not with pure water, but with water containing ammonium oxalate and ammonia. These substances are volatilized in the ignition.

6. Calcium oxalate is practically insoluble in water (5.6 mg. of the anhydrous salt per liter of saturated solution), and only very slightly soluble in acetic acid, but it is readily dissolved by the strong mineral acids. This behavior with acids is explained by the fact that oxalic acid lies about halfway in strength between acetic acid and the strong mineral acids. In acetic acid solution, the hydrogen-ion concentration is too low to appreciably diminish the concentration of $C_2O_4^{--}$ ions, and practically no solvent action takes place. In the solution of a strong mineral acid, however, the high hydrogen-ion concentration causes the calcium oxalate to dissolve according to the following scheme:

$$\left. \begin{array}{c} CaC_2O_4 \rightleftarrows CaC_2O_4 \rightleftarrows Ca^{++} + C_2O_4^{--} \\ \text{(solid) (dissolved)} \\ HCl \rightleftarrows Cl^- + H^+ \end{array} \right\} \rightleftarrows \left\{ \begin{array}{l} HC_2O_4^- \text{ or} \\ H_2C_2O_4. \end{array} \right.$$

The oxalate is immediately reprecipitated from such a solution upon the addition of a base; the hydroxide ions unite with the hydrogen ions of both the mineral acid and the oxalic acid to form water, and the Ca^{++} and $C_2O_4^{--}$ ions left in the solution recombine to form CaC_2O_4. (Compare the precipitation of $Ca_3(PO_4)_2$ from the acid solution of apatite by ammonium hydroxide, in the preceding exercise.)

7. Upon ignition, calcium oxalate becomes anhydrous slightly above 180°, and at low redness it is decomposed into calcium carbonate and carbon monoxide. Strong ignition converts the carbonate into the oxide; in a platinum crucible, this conversion may be carried to completion over a large Meker burner. With porcelain crucibles, however, an electric furnace is to be preferred.

Since calcium oxide absorbs moisture and carbon dioxide from the air, it should be weighed as rapidly as possible.

8. By burning off the filter and then evaporating with 2–3 cc. of 6-normal sulphuric acid, the calcium oxalate may be converted into sulphate, and this may be heated to constant weight. While this procedure is preferred by some analysts, it is nevertheless disadvantageous, since it involves danger of loss by spattering. Moreover, calcium sulphate is more readily decomposed upon ignition than barium sulphate, and there is some danger of loss on this account.

B. **Procedure for the Determination of Magnesium.** Evaporate the acidified filtrates and washings from the calcium oxalate on the steam bath until the salts begin to crystallize. Dilute the solution cautiously with small portions of water, and with stirring, until the salts are brought back into solution, adding a little hydrochloric acid if the solution has been evaporated to a very small volume. (If the *acid* solution contains solid matter at this point, it should be filtered.) Carefully add ammonia to the clear solution, just to alkaline reaction (methyl orange); add sodium ammonium phosphate solution, drop by drop with stirring, as long as a precipitate continues to form, and then 10 cc. in excess. Finally add to the solution one third of its volume of 6-normal ammonia, stir vigorously for 10 minutes, and allow the mixture to stand for at least 6 hours, — preferably overnight.

Decant the solution through a filter, and wash the bulk of the precipitate on to the filter with 2.5 per cent ammonia (one volume of 6-normal ammonia to three of water); do not bother to clean the beaker completely. Dissolve the precipitate from the filter with the least possible quantity of hydrochloric acid (6-normal acid diluted with twice its volume of water), receiving the acid solution in the precipitation beaker. Wash the filter with small portions of hot water until the washings are free from chlorides. Add to the combined filtrate and washings 2 cc. of sodium ammonium phosphate solution and then aqueous ammonia, drop by drop with constant stirring, until the liquid smells distinctly of ammonia. Stir for two minutes, add to the solution one third its volume of 6-normal ammonia, and allow the mixture to stand for 2 hours. Decant the clear liquid through a filter and transfer the precipitate to the filter by means of 2.5 per

cent ammonia. Continue the washing with this liquid until 3 cc. of the washings give no opalescence with nitric acid and silver nitrate.

Dry the filter completely in the covered funnel, and then ignite, taking great pains to raise the temperature very slowly and to insure the presence of plenty of air. Do not raise the temperature above moderate redness until the precipitate is white. Finally ignite to constant weight over the blast lamp or in a muffle furnace. Report the percentage of MgO found.

NOTES. — 1. The filtrates from the calcium oxalate should be slightly acidified immediately after filtration, in order to avoid the solvent action of the alkaline solution upon glass.

2. The precipitation of the magnesium should be made in a small volume of liquid, and the ratio of ammonia to the total volume of solution should be carefully regulated, on account of the relative solubility of the magnesium ammonium phosphate. (Compare Note 6, under the determination of Phosphoric Anhydride.)

3. In the presence of ammonium salts in large quantity, the first precipitate is rarely wholly crystalline; it is apt to contain the mixed phosphate, $Mg[(NH_4)_2PO_4]_2$, which upon ignition leaves magnesium metaphosphate $Mg(PO_3)_2$; and, if produced in the presence of too much ammonia, it may also contain some tri-magnesium phosphate, which upon ignition remains unchanged as $Mg_3(PO_4)_2$. Such precipitates can be purified by dissolving in a very little hydrochloric acid, adding a small quantity of sodium ammonium phosphate, and reprecipitating the magnesium, in the practical absence of ammonium salts, by means of ammonia.

4. In order to avoid a partial reduction of the phosphorus, the precipitate should be heated gently at first, until all the ammonia is expelled and the filter consumed. Also, if heated too soon to a bright red heat, the precipitate becomes glazed over, and it is then impossible to remove the carbon by further heating.

Concerning the use of Munroe or of Gooch crucibles, see Note 8 under the determination of phosphoric anhydride.

## THE DETERMINATION OF CARBON DIOXIDE IN LIMESTONE

Method. The weighed carbonate is placed in an apparatus which contains acid in a separate compartment; the whole apparatus is then weighed. After this the acid is run in upon

the carbonate, and the carbon dioxide set free is removed from the apparatus through a tube filled with calcium chloride, which prevents the escape of moisture from the apparatus. Finally, the apparatus is weighed again, and the loss in weight indicates the quantity of carbon dioxide in the sample.

Many different forms of apparatus have been devised for this purpose. The one shown in the accompanying figure is an improved form of the so-called alkalimeter of Mohr. It consists of a small, wide-mouthed, flat-bottomed flask F, which has a ground-glass connection with the tubes A and B, which are for acid and calcium chloride. The ground-glass joints are lubricated with a mixture of vaseline and beeswax, or other suitable substance.

Procedure. Thoroughly clean the apparatus, allow it to drain, and finally dry it by *gently* heating the flask while drawing a current of dry air through it. As aspirator an inverted washbottle (shown in the figure on a very much reduced scale) may be used, from which the water is caused to run out slowly through the shorter tube. During aspiration the calcium chloride tubes C and D should be connected with c and d, as shown in the figure, so that no moisture may enter the apparatus. After drying the apparatus, place a loose wad of cotton at the bottom of B; introduce into the neck of the tube a cylinder of glazed paper about 3 cm. wide, and through this cylinder pour in small pieces of calcium chloride until the tube is about three fourths full; remove the glazed paper, taking care to keep the upper walls of the tube free from calcium chloride. Place another cotton wad in the tube, insert the stopper, and close the tube temporarily at d by means of a short piece of glass rod within rubber tubing.[1]

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[1] The tube must be kept closed when not in use, to prevent the gradual absorption of moisture from the air. Each of the ordinary calcium chloride tubes previously mentioned is filled in the same way about two thirds full, but in this case a softened cork stopper, pierced by a short piece of glass tubing with rounded ends, is introduced and shoved far into the tube with the help of a stirring rod, leaving the outer 2 or 3 mm. empty. This space in the tube is filled with molten sealing-
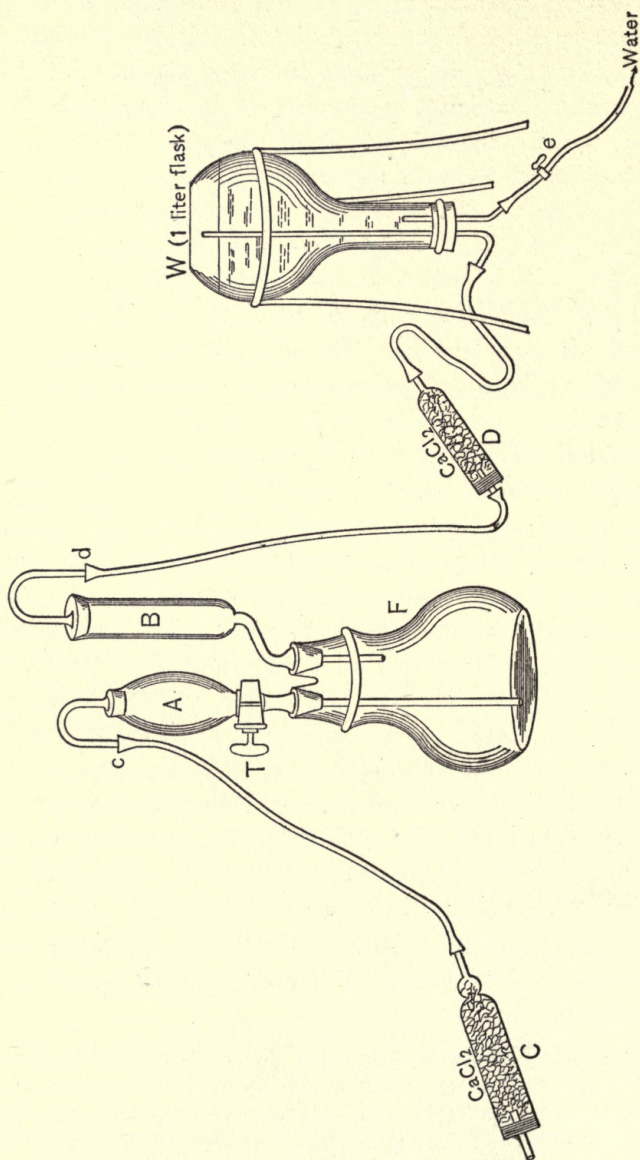
When all is ready, weigh out into the flask about 1.5 g. of the finely powdered substance, which has been dried at 100° C. and allowed to cool in a desiccator, and add 3–4 cc. of water. Close the stopcock *T* and fill the tube *A* about three fourths full with hydrochloric acid (1 volume of 6-normal acid to 1.5 volumes of water) by means of a small funnel. The whole apparatus, with the tubes open at *c* and *d*, is now accurately weighed; the two calcium chloride tubes are connected at *c* and *d*; and the stopcock *T* is slightly opened so that the acid from *A* slowly drops into the flask. As soon as the evolution of carbon dioxide begins to take place quietly, the apparatus is allowed to stand without watching for about half an hour. All of the acid will then have entered the flask, and the decomposition will be practically complete. It now remains to remove the carbon dioxide absorbed by the liquid and contained in the apparatus. To this end, connect the calcium chloride tube *D* with the wash bottle *W*, as shown in the figure (the wash bottle is of course much larger than the figure would indicate), and regulate the flow of water through *e* so that not more than 3 or 4 bubbles of air per second pass through the flask *F*. Then heat the flask *F* gently, by means of a small flame, until the acid just begins to boil; at once remove the flame, and continue to aspirate air through the apparatus until it is cold. Stopper the tubes at *c* and *d*, wipe the apparatus with a clean dry towel, and allow it to stand for one half hour near the balance. Finally, remove the stoppers from *c* and *d*, and weigh the apparatus. Report the percentage of CO_2 found.

Notes. — 1. This method yields excellent results in the estimation of large amounts of carbonic acid such as are present in limestones and baking powders. But it is unreliable for the determination of small quantities, *e.g.* in cements.

2. Since baking powders are decomposed by water, they should be kept dry until after the apparatus has been weighed; and since their efficiency

wax, so that an air-tight connection is made. These tubes also are closed, when not in use, by glass rods within rubber tubing.

as leavening agents depends upon the volume of gas liberated under the conditions of actual usage, water should be placed in the tube A, instead of acid. Otherwise the procedure is the same. The loss in weight is then a measure of the available carbon dioxide of the sample.

3. Carbon dioxide is readily displaced from the apparatus by the method described, but in order to insure its complete removal at least a liter of air should be drawn through the apparatus. The small tube from A should project well below the surface of the liquid, for in order to remove carbon dioxide efficiently from the solution, the air must be made to bubble through the liquid.

4. Since commercial calcium chloride is apt to contain free lime, it should for the best results be treated with carbon dioxide before the determination is made. For this purpose a current of the dry gas is passed through the apparatus for a minute or two, the tubes at c and d are closed, and the apparatus allowed to stand overnight. The carbon dioxide is then removed by aspirating dry air through the apparatus for about 20 minutes, after which the sample may be placed in the flask.

5. The most serious objection to this method is the fact that, owing to the size and weight of the apparatus, there is likely to be an appreciable error in the difference between the two weights. This danger, however, can be largely overcome if a similar piece of apparatus is available as a tare.

THE DETERMINATION OF SILICA IN A REFRACTORY SILICATE

Method. The finely ground sample is fused with an excess of sodium carbonate, whereby it yields sodium silicate and other compounds, depending upon the nature of the mineral. The melt is then decomposed with hydrochloric acid, which should dissolve everything except a portion of the silicic acid. Upon evaporating the liquid, the silicic acid in solution loses water and becomes much less soluble; upon extracting the residue with hydrochloric acid, filtering from silica, and evaporating the filtrate, however, appreciable amounts of silica are recovered in a second filtration, leaving negligibly small amounts in the filtrate. Upon strongly igniting the precipitates, the silica (contaminated with iron oxide and alumina) is left in the anhydrous condition. After weighing, this is evaporated with hydrofluoric acid and a few drops of sulphuric acid, and the

residue is subjected to strong ignition.　The weight of the impure silica less that of the ignited residue gives the weight of the silica originally in the sample.

Procedure.　Grind about 3 g. of the material in an agate mortar until it will entirely pass through a sieve of fine silk bolting cloth.[1]　Weigh out into two platinum or palau (also called rhotanium) crucibles portions of the silicate of about 0.75 g. each.　Also weigh out, on a rough balance, two portions of anhydrous sodium carbonate of about 4 g. each.　In each case, add about three fourths of the sodium carbonate to the silicate sample in the crucible, place the latter on a piece of glazed paper, and thoroughly mix its contents with a dry glass rod.　Place the remaining fourth of the flux on top of the mixture, after first stirring it with the rod to remove from the latter any adhering particles of the mixture.　Cover the crucible and heat it gradually to the highest heat of the Bunsen or Tirrill burner, and then, if necessary to secure complete fusion, heat the mixture over a Meker burner or a blast lamp.　As soon as the mass is in quiet fusion, evolving no gas bubbles, take up the crucible in tongs applied to the upper edge, and, by means of a slow rotary motion, cause the liquid melt to spread around the walls of the crucible, where it will solidify.　As soon as this takes place, and while the mass is still red-hot, plunge the lower portion of the crucible for a few seconds into cold water, but with care not to allow any water to enter the crucible.　Then set the crucible aside to cool. The solid material may then be loosened from the crucible by gentle tapping.　(*Do not deform the crucible.*)

Place the solid melt in a rather tall beaker, add 100 cc. of water and, with stirring, gradually add 50 cc. of 6-normal hydrochloric acid.　Also clean the crucible and lid with a little of the acid, and add this to the main portion in the beaker.　(In case

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[1] Place the ground material in a small beaker and stretch over the top a piece of the bolting cloth, fastening the cloth in place by means of a rubber band below the rim of the beaker.　By gently tapping the inverted beaker over a piece of clean paper, the fine particles are caused to pass through the sieve.　The coarser particles which fail to pass through must be returned to the mortar and reground.

the melt adheres obstinately to the crucible, place both in the beaker and treat with water and acid as described.) Heat the beaker gently, and, if necessary, aid the disintegration of the melt by gentle pressure with the broadened end of a glass rod. After complete disintegration, transfer the mixture to a porcelain casserole, evaporate to dryness on the steam bath, stirring frequently towards the end until the residue is a dry powder. Heat the dry residue on the steam bath for at least an hour, cover it with 5 cc. of 12-normal hydrochloric acid, warm gently, see that the residue is wholly moistened with acid, add 100 cc. of water, and heat to boiling.   Filter promptly, and wash five times with hot dilute acid (1 volume of 6-normal hydrochloric acid to 3 of water), collecting the filtrate and washings in a porcelain casserole; evaporate to dryness, heat the dry residue on the steam bath for one hour, and proceed as before, using a fresh filter to remove the silica.   Wash the filter with hot dilute hydrochloric acid, as before, and then wash both filters with hot water until the washings are free from chlorides.

Transfer both filters to a weighed platinum (or palau) crucible, and ignite cautiously until the paper is consumed, then at the full heat of the burner for half an hour. Moisten the cold residue with 2 or 3 drops of strong sulphuric acid, heat cautiously to expel the free acid, ignite to low redness, and finally for half an hour over the blast lamp.   Repeat the blasting for periods of 5 minutes, to constant weight.

Now add to the silica in the crucible 1 cc. of 6-normal sulphuric acid and 3 cc. of pure hydrofluoric acid.   (This acid should not be allowed to come in contact with the skin, as it produces painful wounds.)   Evaporate as far as possible on the steam bath in a well-drawing hood, adding more hydrofluoric acid if any solid residue remains.   Cautiously fume off the sulphuric acid, heat to low redness, and finally ignite over the blast lamp, for 5-minute periods, to constant weight.   Deduct the weight of this residue from that of the impure silica, and from the difference calculate the percentage of SiO_2 in the sample.

NOTES. — 1. The whole of the sample must be ground very fine, or the coarser particles will resist the action of the flux; unless all of the material is passed through the bolting cloth, the sifted portion may not represent an average sample.

2. Upon fusion with sodium carbonate, silicates are decomposed with the evolution of carbon dioxide. The other products of the decomposition are sodium silicate and aluminate, ferrous carbonate or ferric oxide, calcium and magnesium carbonates, etc. Owing to the evolution of gas during fusion, the heating should be gradual and the crucible should be kept covered.

3. Upon disintegrating the mass with a considerable volume of dilute acid the silicic acid at first largely enters the solution, but upon evaporation it is rendered almost insoluble. Treatment of the fused mass with strong acid would be likely to cause the separation of gelatinous silicic acid which would inclose metallic salts and withhold them from the solution.

4. A gritty residue remaining after the disintegration of the melt with acid indicates that the original silicate has been but imperfectly decomposed. In such a case the fusion should be repeated with another sample, which should be sufficiently well ground and thoroughly mixed with the flux.

5. Silicic acid cannot be rendered wholly insoluble by a single evaporation and heating; nor are repeated evaporations and moistenings before filtration as effective in separating the silica as are alternate evaporations and filtrations. The underlying causes are as yet obscure.

6. To free the silica as far as possible from mineral salts, the residue after evaporation should be thoroughly extracted with warm hydrochloric acid; and the solution should be diluted to a large volume to prevent the inclosure of impurities by the silica. The silica is first washed with dilute acid, to prevent the partial separation of basic salts of iron, aluminum, etc., by hydrolysis; the washing is then completed with hot water.

7. The finely divided silica holds moisture so tenaciously that prolonged ignition over the blast lamp is necessary. Even then the ignited powder tends to absorb moisture, and it should therefore be weighed as rapidly as possible.

8. Notwithstanding all the precautions, the ignited silica is rarely pure. Upon evaporation with hydrofluoric and sulphuric acids, however, the silica is volatilized as silicon tetrafluoride and water, and a sulphate residue is left. If the contaminating substance is an alkali salt, as sodium chloride, the residue will remain as sulphate, even at high temperatures; but certain other sulphates, as those of iron, aluminum, and titanium, evolve sulphur trioxide on ignition and leave the corresponding oxides. In the estimation of silica, the weight of impurities in the silica is always determined by weighing the residue from the hydrofluoric and sulphuric acid treatment;

in order then that the impurities weighed with the silica may be as nearly as possible identical with the residue from this treatment, it is best to treat the silica before ignition with a few drops of sulphuric acid. The final residue from the hydrofluoric and sulphuric acids should also be subjected to the same temperature employed in the ignition of the silica.

9. The procedure for the determination in the united filtrates from the silica of the mixed oxides of iron, aluminum, etc. and of calcium and magnesium, does not differ materially from that given under the determination of calcium and magnesium in limestones.

10. For a thorough study of the analysis of silicate and carbonate rocks, the student is referred to Bulletin No. 422 of the United States Geological Survey, by W. F. Hillebrand.

THE DETERMINATION OF POTASH IN SOLUBLE SALTS

The sample may be a pure salt, a soluble industrial product, or an artificial mixture of potassium chloride and sodium carbonate.

Principle. The determination of potassium by this method depends upon the insolubility of potassium perchlorate, and the solubility of sodium and certain other perchlorates in 96% alcohol. This is not a precipitation method, but one of extraction. If heavy metals are present, they are first removed.

Procedure. Weigh out samples sufficient to contain about 0.25 g. of K_2O, into 50 cc. beakers, and treat each as follows: Warm the sample with 25 cc. of water, and, if sulphates are absent, filter into a 100-cc. porcelain dish; if, however, sulphates are present, acidify with 6-normal hydrochloric acid, stir, treat the hot acid liquid with barium chloride solution in slight excess, filter into a 100-cc. porcelain dish, evaporate the filtrate to dryness on the steam bath, and warm the residue with 15–20 cc. of water, with stirring. Add to the solution sufficient perchloric acid to contain 1.7 times the sample's weight of $HClO_4$ (See Note 2), and evaporate to a sirupy consistency. Add 15 cc. of hot water and 2 cc. of perchloric acid, and again evaporate. Once more add 15 cc. of hot water, and evaporate until heavy fumes of perchloric acid appear.

Allow the mixture to cool thoroughly, add 20 cc. alcohol containing 0.2% by weight of $HClO_4$,[1] and stir for some time, keeping the salt as coarsely granular as possible. Let settle, decant the liquid through a weighed Gooch crucible [2] (containing a mat moistened with the wash liquid), and to the residue add a second 20-cc. portion of the wash liquid. Stir, let settle, again decant, and then drive off the remaining alcohol on the steam bath. Dissolve the residue in 15 cc. of hot water, add a few drops of perchloric acid, and evaporate to heavy fumes. Cool, add 1 cc. of the wash liquid, decant, and test a few drops of the washings for complete extraction. (The extraction with the alcoholic liquid must be continued until a few drops of the filtrate leave no residue when evaporated to dryness on platinum foil.) Finally, cool, add 1 cc. of the wash liquid, and sweep the salt into the Gooch crucible with a policeman, washing at last with a very little pure 96% alcohol. Dry the salt for half an hour at 130°, and weigh.

Report the percentage of K_2O in the sample.

Notes. — 1. This method was proposed in 1831 by Sérullas, but, owing to some mistaken ideas concerning the properties of perchloric acid, the proposition did not receive the attention it deserved. Perchloric acid solutions of satisfactory grade can now be obtained in the market, they can be kept indefinitely in glass-stoppered bottles, and the method rivals in results the chloroplatinic acid process; and this at a greatly reduced cost.

2. The specific gravities of perchloric acid solutions are as follows: 70% $HClO_4$, 1.67; 60% $HClO_4$, 1.54; 50% $HCLO_4$, 1.41; 30% $HClO_4$, 1.20; 20% $HClO_4$, 1.12. The strength of a solution of the pure acid may easily be determined by the dilution of a known amount and titration with sodium hydroxide, with phenolphthalein as indicator.

3. In order to obtain the potassium as pure $KClO_4$ by this method, it is essential that no strong acids be present, other than perchloric acid, which yield salts insoluble in alcohol. Sodium chloride and sulphate are such salts, and it is therefore necessary to remove chlorides and sulphates before

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[1] Made by mixing 1.7 cc. of the 60% acid, or 4.4 cc. of the 30% acid, with one liter of 96% alcohol.

[2] It is better to use a Munroe crucible, with a filter of platinum sponge. The crucible itself may be of gold, to save expense.

the treatment with alcohol. HCl may be removed by repeatedly evaporating the aqueous solution with the less volatile $HClO_4$; but H_2SO_4 is less volatile than $HClO_4$, and cannot be expelled in this way. Before the first evaporation, therefore, the latter should be precipitated from the hot acid solution by means of $BaCl_2$ in slight excess. Phosphates, though often insoluble in alcohol, need not be removed; but, in their presence, a larger excess of $HClO_4$ should be used, to insure their complete removal by the wash liquid, as H_3PO_4. (See Note 5 of this procedure, and also Note 6 under the determination of calcium.)

4. Since NH_4ClO_4 is only sparingly soluble in alcohol, ammonium salts should be carefully expelled by gentle ignition, before the treatment with $HClO_4$. Moderate amounts of barium, calcium, and magnesium do not interfere with the procedure; their perchlorates are soluble in alcohol.

5. The perchlorate mixture is extracted with alcohol containing a small amount of $HClO_4$ because, owing to the common ion effect, the solubility of $KClO_4$ is less in it than in pure alcohol; the two solubilities are about 4 mg. and 16 mg. per 100 cc., respectively. The solubility of $KClO_4$ is still less in the presence of sodium, and other soluble perchlorates; *i.e.* in the first portions of the alcoholic extract. Alkali and alkali-earth phosphates are decomposed by perchloric acid and the H_3PO_4 dissolves in the acid-alcoholic liquid; in the presence of phosphates, therefore, perchloric acid should be present in considerable excess.

6. If a known weight of NaCl—KCl mixture, obtained for example in a silicate analysis, is converted into a mixture of the perchlorates, and the $KClO_4$ isolated and weighed, the method yields both the K_2O and Na_2O contents of the original sample. (Cf. Part IV, Problem 29.)

7. In order to prevent the loss of $KClO_4$, in the separation of sodium and potassium, it has been suggested to extract the perchlorate mixture with an alcoholic liquid which has previously been saturated with $KClO_4$. This procedure, however, is apt to lead to high results, owing to the precipitation of small amounts of potassium from the wash liquid by the $NaClO_4$ entering into solution; it is therefore not to be recommended. In order to obtain exact results, it suffices to avoid the use of unnecessary quantities of the wash liquid.

THE ELECTROLYTIC DETERMINATION OF COPPER

The sample to be analyzed may be pure copper sulphate, an artificial mixture of the carbonates of copper and sodium, a copper ore, or a nickel coin. In case stationary electrodes are employed, the solution should contain not over 0.2 g. of copper

and 5 cc. of nitric acid (sp. gr., 1.42), and should have a volume of 100 cc.; in the case of a rotating anode, however, the solution may contain as much as 0.5 g. of copper, and it should contain, in a volume of 100 cc., 3–5 cc. of nitric acid (sp. gr., 1.42), or 1 cc. of sulphuric acid (sp. gr., 1.84) and 3 g. of ammonium sulphate.

Method. The copper salt is decomposed by the electric current, and the copper deposited upon the cathode (negative electrode). The cathode is weighed before and after the operation, and the increase in weight indicates the quantity of copper in the sample.

The polarity of the terminals may be determined by bringing the wires, about 0.5 cm. apart, into contact with a piece of filter paper moistened with potassium iodide solution. At the positive terminal iodine will separate and color the paper.

Cleaning the Platinum Electrodes.[1] The electrodes are freed from grease by heating with dilute sodium hydroxide solution, after which they are washed with water; the cathode is then dried, allowed to cool in a desiccator, and weighed. To clean the *platinum* cathode after the determination, cover the deposit completely with 6-normal nitric acid, heat for at least 15 minutes, and wash.

A. **Procedure with Stationary Electrodes.**[2] Dissolve a 0.5–0.6-g. sample of copper sulphate, $CuSO_4 . 5 H_2O$, in 50 cc. of water, in a tall 150-cc. beaker; stir to complete solution, add 4 cc. of nitric acid (sp. gr., 1.42), and dilute to 100 cc. Immerse the electrodes in the solution and connect them in such a way that the electrode with the larger surface is made the cathode. The electrolysis, which should be carried out at a potential of 1.9–2.0 volts, may be completed in the cold over night, or in two or three hours if the temperature is kept at 70–80° by means of a heated sheet of wire gauze placed a short distance below the beaker. Finally test for complete deposition by adding a little water to raise the level of the solution on the

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[1] In case a silver cathode is used, see Note 12.
[2] If the sample is an ore, see Note 11.

cathode; if after 30 minutes no copper is to be seen upon the fresh platinum surface, the deposition is probably complete. (Test a few cubic centimeters of the solution with sodium acetate and a drop of potassium ferrocyanide solution.) Without disconnecting the electrodes, siphon off the electrolyte while introducing distilled water, until the current ceases to pass; this is to prevent the re-solution of any of the copper by the acid liquid. Remove the cathode, wash it with water, then with alcohol, and dry it for a short time in an air bath at 85–90°. Allow the cathode to cool in a desiccator, and weigh.

B. **Procedure with a Rotating Anode.**[1] Heat a five-cent coin with sodium hydroxide solution to free it from grease, then wash it with water, and dry at 100°. After cooling, weigh the coin, and dissolve it in 50 cc. of 6-normal nitric acid, in a covered casserole. Evaporate the solution to dryness on the steam bath, dissolve the residue in about 100 cc. of cold water, add 10 cc. of sulphuric acid (sp. gr., 1.84), allow to cool, and transfer the whole to a 500-cc. measuring flask, diluting to the mark with water. Measure off one tenth of the well-mixed solution into a 50-cc. graduated flask and transfer this quantitatively to the electrolytic vessel; before transferring the solution to the electrolytic vessel, however, pour 100 cc. of water into the latter and adjust the electrodes so that, when four fifths covered with water, they do not come into contact with one another, nor cause a loss of liquid, when the anode is rotated. The water can then be siphoned, or drawn off, and the solution transferred to the vessel and diluted to 100 cc. without disturbing the vessel or the electrodes.

To perform the electrolysis, attach the anode to the shaft of the rotator (which is connected by means of a mercury cup, or otherwise, with the positive terminal), and the cathode to the negative terminal. Adjust the levels so that, with 100 cc. of solution, the cylindrical cathode is about four fifths immersed in the liquid. Then, by means of the sliding contact,

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[1] If the sample is an ore, see Note 11.

throw in the maximum resistance of the rheostat, see that all connections are well made, start the motor, and close the switch; immediately decrease the resistance of the rheostat until the ammeter registers about 1 ampere, and allow the electrolysis to proceed. *In the presence of nickel, the voltage should not exceed 2.7.* After about 55 minutes, test for complete deposition by adding a little water to raise the level of the solution on the cathode; if after 10 minutes no copper is visible on the freshly exposed platinum, the deposition is complete. When this is the case, without disconnecting the terminals, stop the rotator and draw off the solution into a large beaker, carefully pouring in water as fast as the solution flows out.[1] As soon as the ammeter indicates that no current is passing, throw off the switch, remove the cathode and wash off the water with a little alcohol; dry below 100°, allow to cool in a desiccator, and weigh.

NOTES. — 1. If two platinum plates, immersed in an aqueous solution of copper sulphate, are connected by wire with the poles of a storage battery, metallic copper will be deposited upon one of the plates; under certain conditions, all of the copper will separate in the form of a compact, firmly adherent metallic film.

The process of decomposition is called *electrolysis;* the solution undergoing decomposition is called an *electrolyte;* the two poles by which the current enters and leaves the electrolyte are called *electrodes.* When salt solutions are electrolyzed, the positive ions (cations) move towards the negative electrode (cathode), and the negative ions (anions) towards the positive electrode (anode).

The quantity of electricity which passes through the solution in unit time, or the speed of the current, is measured by an *ammeter.* The unit,

[1] If it is desired to determine the nickel electrolytically, evaporate this dilute solution to a volume of 25–30 cc., make slightly alkaline with ammonia, filtering off any ferric hydroxide which may be precipitated, and to the solution (40 cc. in volume) in the electrolytic vessel add 60 cc. of ammonia of sp. gr. 0.90. Electrolyze at 3.0–3.5 volts with a rotating anode. After about an hour, test for complete deposition by adding to a few drops of the solution, neutralized with acetic acid, a drop or two of dimethyl-glyoxime solution (a red color indicates nickel). When the deposition is complete, proceed as directed in the copper determination. Finally remove the nickel from the cathode by heating for at least 15 minutes with 6-normal nitric acid.

called an *ampere*, is represented by the unvarying current which, when passed through a solution of silver nitrate, deposits metallic silver at the rate of o.oo1118 g. per second.[1]

The electromotive force, *i.e.* the electrical pressure which drives the current along the circuit, is measured by the *voltmeter*. The unit, called a *volt*, is represented by the electrical pressure that produces a current of one ampere when steadily applied to a conductor whose resistance is one ohm.

The unit of resistance, called an *ohm*, is represented by the resistance offered to an unvarying electric current by a column of mercury 14.4521 g. in mass, of a constant sectional area and a length of 106.3 cm., at the temperature of melting ice.

These magnitudes are always related to one another as follows (Ohm's law):

$$\text{Quantity of electricity (amperes)} = \frac{\text{Electromotive force (volts)}}{\text{Resistance (ohms)}}, \text{ or } i = \frac{E}{R}.$$

The most satisfactory current producer for electro-analysis, in which a steady non-fluctuating current is desired, is the secondary or storage element. The E. M. F. of the lead cell is about 2 volts, and the necessary voltage for the work may be obtained by connecting several cells in series. In practice, the potential difference between the electrodes is regulated by means of incandescent lamps, coils of wire, or other devices, which offer resistance to the flow of electricity along the circuit and convert electrical energy into heat. Any rheostat will do for this work, provided the range in resistance is properly related to the other factors which determine the current strength. The sliding-contact coil resistances which are on the market are very satisfactory. Voltmeters and ammeters should have the scales graduated with a range as limited as is consistent with the current conditions to be employed, so that each subdivision may represent a small fraction of a unit. The manner of connecting the instruments is illustrated in the accompanying figure.

2. The passage of an electric current of suitable voltage through the solution of an ionogen is associated with physical and chemical changes which often may be utilized in exact gravimetric analysis.

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[1] The quantity of a given metal deposited by a current of electricity is directly proportional to the quantity of electricity which passes through the solution; and the quantities of different metals deposited by a specific quantity of electricity are directly proportional to the chemical equivalents of the metals in the solution. These two statements are known as *Faraday's laws*, though these apply to non-metallic ions as well.

The chemical effect at the cathode is always some form of reduction. Simple metallic ions, as those of copper, tin, nickel, cobalt, cadmium, etc., travel towards the cathode, where they give up their charges and separate
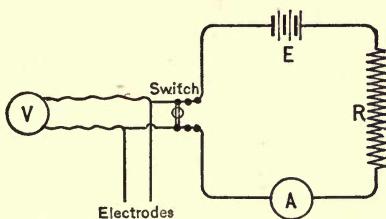
in the metallic condition; while the hydrogen ion here loses its positive charge and either acts directly as a reducing agent (*e.g.* nitric acid to ammonia) or is evolved as gaseous hydrogen.

At the anode, on the other hand, the chemical effect is always some form of oxidation. The anions of the halogen group are liberated as free chlorine, bromine, or iodine and may act as oxidizing agents, while from solutions containing hydroxide, sulphate, or nitrate ions, oxygen separates at the anode and either acts directly as an oxidizing agent or is evolved in gaseous form. (It should be borne in mind in this connection that aqueous solutions always contain the ions of water.) Although positive ions always move towards the cathode, certain metals (*e.g.* lead, cobalt, nickel, and a few others) may, under specific conditions, be oxidized (possibly to complex oxy-anions) and deposited more or less completely at the anode in the form of insoluble peroxides. In fact, lead can be determined accurately in this way, as an oxide.

3. Metals, like all other substances, possess when immersed in water a characteristic solution tension, by which is understood an expansive force which seeks to drive particles of the metal into the solution; when a metal is immersed in the solution of one of its salts it will either send more of its atoms into the solution as ions, or some of its ions will be discharged from the solution on its surface as atoms. In the first case the metal will become negatively charged, and in the second case positively charged with respect to the solution; in either case equilibrium will be reached when the solution tension of the metal is exactly counterbalanced by the electrostatic charges and the osmotic pressure of the metallic ions in the solution.

Upon comparing the different elements from the standpoint of the potential difference between them and their salt solutions, at identical normal ion-concentrations, a characteristic series of values is obtained.

In the case of solutions of normal ion concentration, for example, some of the values are as follows:

$$Zn = +0.493 \qquad Ag = -1.05$$
$$Cd = +0.143 \qquad I = -0.80$$
$$Fe = +0.067 \qquad Br = -1.27$$
$$Co = -0.045 \qquad O = -1.50 \quad \text{(At } N. \text{ H}^+\text{-ion concentration.)}$$
$$Ni = -0.049 \qquad Cl = -1.63$$
$$H = -0.277 \qquad SO_4 = -2.18$$
$$Cu = -0.606$$

4. In the electrolysis of a salt solution, both electrodes soon become coated with the products deposited (*i.e.* each becomes essentially an electrode of the deposited material, no matter what its original composition) and they are said to be polarized. Hence a system similar to that just discussed may be considered to exist at each electrode, and it is evident that electrolysis must act in opposition to the solution tension of the elements and in conjunction with the osmotic pressure of their ions. In order then to decompose a salt solution continuously, a voltage at least slightly in excess of the polarization voltage must be applied; *i.e.* a voltage greater than the numerical difference between the single potential differences normally established at the cathode and anode. Assuming normal ion-concentrations, the decomposition voltage of copper chloride, for example, is -1.63 minus $-0.606 = 1.02$ volts; but the decomposition voltage of a solution as calculated in this manner, especially in the case of a salt of an oxyacid, frequently fails to agree with that found by experiment. The separation of gases at the electrodes is often accompanied by "overvoltages," which vary more or less markedly with the material and physical nature of the electrodes; moreover, the ion-concentration is generally unknown, and it always changes as the electrolysis proceeds. The important matter here lies not so much in the calculation of decomposition voltages as in the recognition of the existence of a minimum decomposition voltage for every ionogen, under definite conditions.

In the case of an ionogen of known decomposition voltage, we should simply use a somewhat higher voltage, but if other metallic ions were present it might be impossible to completely deposit one metal without using a voltage that would start the deposition of the second metal also. While copper can readily be separated from cobalt or from nickel by electrolysis, it is not possible to separate nickel from cobalt in this way; and in general only metals whose deposition voltages differ by several tenths of a unit can be separated from each other by maintaining an intermediate voltage during the electrolysis.

The addition of certain reagents, as ammonia, potassium cyanide, ammonium oxalate, etc., to solutions containing two metals sometimes reduces the concentration of one metallic ion very much more than that of the other, owing to the formation of more or less stable complexes, and makes it possible to perform a separation by the "constant voltage" method that otherwise might not be possible.

5. The current strength will of course depend upon the voltage used, since, according to Ohm's law, $i = \dfrac{E}{R}$. In performing an electrolysis, the voltage actually available is diminished by the decomposition voltage of the electrolyte (polarization voltage); hence the current which passes is equal to the available voltage minus the decomposition voltage of the electrolyte, divided by the resistance of the circuit.

6. The quantity of metal deposited in a given time is dependent upon the strength of the current in amperes. A current of 1 ampere is capable of depositing 1.118 mg. of silver, and, according to Faraday's law, equivalent amounts of other elements, per second. This law might be used to calculate the time necessary for the complete deposition of the metal if, under the analytical conditions, it were the only cation taking part in the electrolysis. In the neighborhood of the cathode, however, the concentration of the solution with respect to this cation gradually decreases to an infinitesimal value, and the resistance and the decomposition voltage of the solution therefore rise; finally a point is reached at which other ions begin to be discharged. Since circulation of the solution tends to maintain a uniform distribution of the ions, mechanical stirring favors the rapid deposition of those ions which have the lowest discharge voltages.

7. Unless the solution is mechanically stirred, the rate of deposition of a given metal decreases rapidly, owing to the decreasing concentration of its ions around the cathode and to the continually increasing proportion of the current which is carried by the hydrogen (or other) ions. Since a rapid circulation of the solution tends greatly to prevent the local decrease in metallic ion concentration around the cathode, and since with improved circulation currents of much higher density may be used than would otherwise give satisfactory deposits, it is possible to greatly reduce the time necessary for a determination by performing the electrolysis with the use of a rotating electrode.

8. Owing to the reduced viscosity at higher temperatures, the resistance offered by an aqueous solution to the passage of electricity decreases with a rise in temperature, and in this way the voltage required to produce a given current may be reduced to a minimum; this may sometimes be of importance in electrolytic separations. Moreover, in case stationary

electrodes are used, heating the solution during electrolysis gives rise to more or less rapid convection currents, and also increases the speed of diffusion, and these effects are equivalent to a gentle mechanical stirring. The solution should never be heated to the boiling point, however, since the deposit might in that case be loosened from the cathode.

9. The deposited metal tends to redissolve in the electrolyte (cf. "polarization"), and consequently the rate at which the metal is deposited must exceed that at which it redissolves. The metal is only deposited from the solution in immediate contact with the cathode, so that the greater the area of the cathode, the more metal there is available for deposition; but also the greater the rate of re-solution. Hence it follows that the current strength necessary for the satisfactory deposition of the metal is proportional to the area of the cathode.

The current strength per unit area is called the *current density;* a square decimeter is generally taken as the unit area. Hence a "normal current density of 2 amperes" means a current of 2 amperes per 100 sq. cm. of cathode area, or of 1 ampere for 50 sq. cm. of cathode area, etc. While the tendency of a metal to redissolve fixes a lower limit for the current density to be used, a higher limit is set by the tendency of the metal to form spongy, non-adherent films when deposited too rapidly.

It is highly important for accurate work to deposit the metal in the form of a compact film which can easily be washed and weighed without loss. The condition of the deposit depends not only upon the current density used, but also upon the concentration of the metallic ions in the solution, the amount of free acid and other substances present, the temperature, etc. The best conditions for specific cases have been determined by repeated experiments.

10. Concerning the effect upon the nature of the deposit of the products that accumulate in the solution during an electrolysis, that are purposely added to the solution, or which were originally present in the sample, it may be stated that a very marked influence is often exerted by certain acids, bases, and other substances. A solution of copper sulphate, if electrolyzed without the addition of another substance, is almost sure to give a reddish brown, non-adherent deposit of spongy copper; the addition of a little sulphuric acid gives rise to a much more compact deposit, while the addition of nitric acid leads to a still better deposit of bright red firmly adherent metal. A small quantity of urea, in addition to either acid, appears to favor still more the formation of a satisfactory deposit. On the other hand, high current densities, which cause a rapid discharge of hydrogen, are apt to yield loosely adherent deposits of spongy metal. A current density which gives a bright red, coherent deposit of pure copper when no

interfering substance is present, will often give a very dark, loosely adherent deposit when arsenic is present, even in small amount. Such impurities must be removed before the electrolysis is begun.

11. If the sample to be analyzed by this method is a copper ore, and is not known to be free from arsenic and other interfering substances, it should be subjected to special treatment, in order to obtain a solution suitable for electrolysis. In most cases, a satisfactory solution may be prepared according to the procedure detailed under the volumetric estimation of copper (which see); the ore is evaporated with aqua regia, the residue extracted with dilute hydrochloric acid and water, and the copper, arsenic, etc., precipitated with sodium thiosulphate; the arsenic is then driven off by ignition, the residue evaporated to dryness with nitric acid, and finally taken up in 4 cc. of nitric acid (sp. gr., 1.42) and 50 cc. of water. This solution is diluted to 100 cc. and electrolyzed.

12. The electrode material should preferably be insoluble in the electrolyte, with or without current action, and for that reason platinum is most often used for electrodes; but the continued advance in the price of this metal has led to a search for less expensive materials. Other metals, as silver and copper, are in some cases suitable for use as cathodes in the deposition of metals (as is also the more expensive palladium-gold alloy which is in the market), but the anode must still be made of platinum or of something equally resistant. In the determination of copper, for example, a silver cathode is about as satisfactory as one of platinum; the deposit can be removed by means of dilute hydrochloric acid, with the addition of a little hydrogen peroxide or nitric acid, and, after washing with ammonia, the cathode is again ready for use.

Since a practical limit is placed upon the current density, the time necessary for a deposition is inversely proportional to the area of the cathode; for this reason the electrode to receive the deposit should present the maximum of surface to the solution.

The platinum dish electrode designed by Classen is quite thin and presents a relatively large surface; a Classen dish weighing 40 g. has a capacity of about 250 cc. and presents an inner surface of about 150 sq. cm. to the solution. A platinum disk or a flat spiral of platinum wire may be used as the anode. The electrodes commonly used, however, are more economical. They are open cylinders of thin foil or of fine mesh gauze, and elongated spirals of heavy platinum wire; the cylinders, which are used to receive the deposit, weigh 10–12 g. and the wire spirals about 8 g. Of all cathodes, those of gauze are the most efficient; they present a relatively larger surface, all parts of the surface are equally effective, they permit a much better circulation of the solution and consequently the use of higher current den-

sities. These cylindrical cathodes and spiral anodes are the ones assumed in the foregoing procedures.

13. In case the electrolysis is to be performed with stationary electrodes, it is best to use a tall beaker of small diameter, which can be heated. If heating is not desired, however, or if a rotating electrode is used, the most suitable vessel is a 150-cc. glass cylinder, with a rounded bottom ending in an outlet tube provided with a stopcock ; the electrodes should reach nearly to the bottom of this cylinder, to insure efficient mixing. After the deposition is complete, without interrupting the current, the electrolyte can easily be drawn off with the simultaneous introduction of distilled water above.

PART III

VOLUMETRIC ANALYSIS

GENERAL DISCUSSION

Fundamental Principles. It has already been pointed out in Part I that in volumetric analysis the amount of an element or compound present in a sample is calculated from the volume of some reagent of known concentration which is required, after suitable treatment of the sample, to complete a definite reaction.

The analytical balance is equally requisite as a starting point for both gravimetric and volumetric systems; in addition to the balance, volumetric processes demand graduated measuring instruments and *standard solutions* (*i.e.* solutions of accurately known value). The concentration or value of a solution for a specific reaction is determined by a procedure called *standardization*, in which the solution is brought into reaction with a definite weight of a substance of known purity; from the volume of solution required to complete the reaction, the strength or value of the solution can be calculated, and it is then a *standard solution*.

The value of standard solutions may be expressed in terms of the weight of reagent actually present in each cubic centimeter, or, better, in terms of the weight of a given substance with which one cubic centimeter of the solution will react; but since the weight of reagent present in a unit-volume is always chemically equivalent to the weight of substance with which the unit-volume reacts, it is in general more convenient to express the value of the standard solution in terms of chemical equivalents per unit-volume. Such solutions are often made to bear some simple

relation to a *normal solution* of the specific reagent; they are, for example, half-normal, tenth-normal, or fiftieth-normal solutions. A *normal solution* contains in one liter one gram-equivalent of the active reagent; *i.e.* that quantity of the active reagent which contains, unites with, replaces, or in any way, directly or indirectly, brings into reaction 1.008 g. of hydrogen.

Thus a liter of *normal acid solution* will contain 1.008 g. of available hydrogen ion (*e.g.* one mol of HCl, or one half mol of H_2SO_4, etc.); and a liter of *normal alkali solution* will contain sufficient available hydroxide ion to combine with 1.008 g. of hydrogen ion, or 17.008 g. (*e.g.* one mol of NaOH, one half mol of $Ba(OH)_2$, etc.). A normal solution of an *oxidizing agent* will have the same oxidizing value per liter as one gram-equivalent, 8.00 g., of oxygen (*e.g.* one sixth mol of $K_2Cr_2O_7$, etc.); and a liter of *normal reducing agent* will have the same reducing value as 1.008 g. of hydrogen (*e. g.* one half mol of $SnCl_2$). It will be seen that a liter of normal acid solution will exactly neutralize a liter of normal alkali solution, and a liter of normal oxidizing solution will exactly oxidize a liter of normal reducing solution, and so on.

It should be especially noted, however, that the equivalent or *normal weight* of a substance may vary according to the reaction in which it is used. Thus the normal weight of oxalic acid is one half its molecular weight, whether it be used as a neutralizing, a reducing, or a precipitating agent; whereas the normal weight of nitrous acid would be the molecular weight, if used either as a neutralizing agent or to oxidize hydriodic acid, but only one half the molecular weight if used to reduce potassium permanganate. In the case of potassium permanganate, two molecules yield three atoms of available oxygen (equivalent to six hydrogen atoms) in neutral solution, and five atoms of available oxygen (equivalent to ten atoms of hydrogen) when used in acid solution. The normal weight of this compound as an oxidizing agent is therefore one third or one fifth of the molecular weight, according to the conditions of its use.

The preparation of *exactly* normal, half-normal, or tenth-normal solutions generally requires considerable time and care, and is usually carried out only when a large number of analyses are to be made, or when the analyst has some other specific purpose in view. It is much easier to prepare standard solutions which differ but slightly from half-normal or tenth-normal, and these still have the advantage of approximate equality; two approximately half-normal solutions are much more convenient to work with than two which are widely different in strength. When these approximate solutions are used, the volumes can readily be reduced to the corresponding values in terms of solutions which are exactly normal, half-normal, or tenth-normal. For example, 25.75 cc. of a 0.0987 N solution are equivalent to $25.75 \times 0.0987 = 2.542$ cc. of the normal, or to $2.542 \times 10 = 25.42$ cc. of the tenth-normal solution.

Reactions Suitable for Volumetric Processes. Volumetric processes are usually based upon definite chemical reactions, and in general only such reactions are suitable as can be made to take place completely and very rapidly when equivalent amounts of the reacting substances are brought together. Volumetric determinations, however, do not always consist in the direct titration of the substances under investigation. In many cases an excess of the standard solution is used, and this excess is then titrated with a second standard solution. The volumetric relation between the two standard solutions being known, the proper correction for the excess of the first solution is easily made. This is known as the method of *back titration*. In other cases the substance under investigation is capable under suitable conditions of setting free or of carrying down as a precipitate a definite proportion of some other substance which can subsequently be titrated with a standard solution; from the volume of the latter required it is an easy matter to calculate directly the weight of the original substance.

The processes of volumetric analysis are readily classified, according to their character, into:

A. Neutralization Methods; such as those of acidimetry and alkalimetry.

B. Methods of Oxidation and Reduction; as exemplified in the determination of ferrous iron by oxidation with potassium permanganate.

C. Precipitation Methods; as, for example, the titration of silver with potassium thiocyanate solution.

Determination of the End-point. In order to utilize a reaction for volumetric purposes, it is necessary to have some means of ascertaining the point at which an equivalent volume of the standard solution has been added. In the neighborhood of this point certain physical and chemical properties of the solution change very rapidly; in many cases there is a marked change in color, electrical conductivity, or oxidation potential of the solution, and in some a precipitate just ceases to form. In numerous cases the presence of another reagent, called an *indicator*, gives rise to a decided color change in the solution, or in a few instances it causes a precipitate to form and thus renders the solution turbid. The point at which the standard solution has been added in sufficient quantity to make these changes apparent is called the *end-point* of the titration. If the process is to be sufficiently accurate, the difference between this point and the true end-point of the reaction (*i.e.* the point at which an equivalent quantity of the solution has been added) must be exceedingly small; and this is actually the case in nearly all of the established volumetric processes.

In a few cases, however, a principle which can be used to great advantage is that of compensating errors; here the errors which are involved in the actual determination are counteracted by equal errors in the standardization of the solution used. Assuming that there is a noticeable discrepancy between the true and the observed end-point, it will generally hold good that this discrepancy will remain constant so long as the conditions are the same. If the solution can be standardized under conditions identical with those which obtain in the actual determination,

all errors can be practically eliminated; the standard solution becomes merely an instrument for comparing two solutions of the same substance, one representing a known amount of the standard solution and the other an approximately equal but unknown amount. Considered from this point of view, whenever it is possible to use the same reagent for the determination of different substances, strict accuracy would demand that the solution be standardized by comparison with a known weight of the substance for which it is to be used in a given case.

General Theory of Indicators. Whenever a substance is titrated in the presence of an indicator, the physical change which enables us to recognize the end-point is the visible result of a chemical reaction in which the indicator itself is an active reagent. In case the indicator is acted upon by the standard solution employed in making the titration, the reactions involved may be represented by the following equations, in which X represents the substance being titrated, R the reagent in the standard solution, and I the indicator employed:

$$(1) \quad X + R \rightleftarrows RX,$$
$$(2) \quad I + R \rightleftarrows IR,$$
$$(3) \quad IR + X \rightleftarrows RX + I.$$
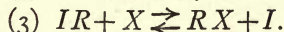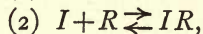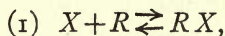
The appearance of the end-point is here dependent upon the concentration of IR,[1] which should remain equal to zero as long as an appreciable amount of X is present, but should increase in direct proportion to the amount of R that is added after the concentration of X has been reduced to an infinitesimal value. In other words, reaction (1) must be completed before reaction (2) begins to take place, but reaction (2) must take place promptly from left to right, even at an exceedingly low concentration of

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[1] IR is not necessarily a compound of the indicator with R, but even so a definite concentration of the free reagent R must finally be present in the solution in order to produce the visible change which is characteristic of the indicator. In such cases reaction (2) may be written $I_1 \rightleftarrows I_2$, and the appearance of the end-point is dependent upon the concentration of I_2, which in turn depends upon that of R in the solution.

R; also, the least possible concentration of IR should cause a marked change in the appearance of the solution. It is further necessary that the small amounts of IR which are formed locally during the titration, in consequence of imperfect mixing, should react with X according to equation (3), thus preventing the appearance of false end-points. This will of course insure the completion of the reaction of X with R before the indicator begins to be permanently influenced by R. It will be seen, therefore, that the closeness of agreement between the observed and the true end-point in any specific case will depend upon the relative magnitudes of the three equilibrium constants concerned, as well as upon the experimental conditions, *e.g.* the concentration of the indicator, the temperature, etc.

If, on the other hand, the indicator added reacts with the substance undergoing titration, the reactions concerned must take place essentially according to the following equations:

$$(a) \quad X + I \rightleftarrows I X,$$
$$(b) \quad X + R \rightleftarrows R X,$$
$$(c) \quad I X + R \rightleftarrows R X + I.$$
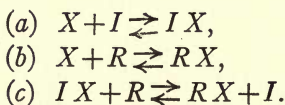
The appearance of the end-point is here dependent upon the final completion of reaction (c) from left to right. The accuracy of the process in any given case will depend here also upon the relative magnitudes of the three equilibrium constants, and upon the experimental conditions. In a few cases, in which $I X$ will not react with R, it is necessary to use a special procedure; as the end-point is approached, the solution undergoing titration is frequently tested, one drop at a time on a white test-plate, with a drop of the indicator solution.

A factor which is usually of great importance in volumetric analysis is the concentration of the indicator in the solution. In those cases in which the end-points obtained depend upon a change from one specific color to another, the two colors may tend to mask one another and give rise to a series of indeterminate transition tints. It is then desirable that the entire

amount of indicator present should be promptly transformed by the slightest possible excess of the titrating solution; in such cases only a very slight amount of the indicator should be used.[1] If, however, the solution containing the indicator is colorless, and the addition of an excess of the standard solution produces a specific color, a relatively larger amount of indicator is less likely to be harmful; in some cases, in which IR is a substance subject to dissociation, it is necessary, in order by mass action to insure its prompt formation, to add the indicator in considerable amount. (Cf. the use of starch in iodometric methods, and also the use of ferric alum in the titration of silver with thiocyanate solutions.)

The Advantages of the Volumetric System. Volumetric determinations can usually be carried out much more rapidly and conveniently than the corresponding gravimetric processes. The actual titration requires a few minutes only, but the necessity of removing interfering substances and of transforming the substance itself into a form suitable for titration often increases the time of the analysis to several hours. In many cases volumetric processes are more accurate than the corresponding gravimetric processes, but in other cases the reverse is true. Volumetric processes often avoid the errors which are involved in making gravimetric determinations; that is, the errors resulting from solubility, from the contamination of precipitates, and from actual mechanical losses. On the other hand they necessarily involve certain errors in the preparation and measurement of the standard solutions (see, however, what is said in Part I concerning the use of weight burettes) and in the determination of the end-points of the reactions which are utilized.

General Directions. For successful volumetric work it is essential that uniformity of practice prevail throughout with

[1] In the case of methyl orange, for example, the indicator is prepared by dissolving 0.02–0.03 g. of the solid compound in 100 cc. of water, and in any one titration only about three drops of this solution should be used. Counting 20 drops to 1 cc., and using 3 drops in a titration, the amount of methyl orange actually present is less than 0.05 mg.

respect to all matters which can influence the accuracy of measurement of liquids. For example, whatever time is allowed for drainage in the calibration of a measuring vessel, should also be allowed whenever the vessel is used; and parallel conditions should be insured during both standardization and analysis, with respect to the quantity of the indicator and the final volume of the reaction mixture after titration. In some cases the standard of the solution will vary appreciably with variation of the experimental conditions.

It is of course necessary that standard solutions should be protected from concentration or dilution; they should be kept stoppered and away from direct sunlight or heat. The bottles should be shaken before use to collect any water that may have evaporated from the solution and condensed on the sides, and, after use, before replacing the stoppers, the necks and stoppers of the bottles should be wiped dry with a clean, lintless towel.

Needless to say, the measuring vessels must be clean and free from grease, and great care must be taken to thoroughly rinse out all burettes and pipettes with the standard solutions they are to contain, in order to remove all traces of water or other liquid, which would act as a diluent. It is best to rinse them three times with small portions of the solution, allowing each portion to run out through the tip, before assuming them to be in a condition to be filled and used.

Much time may be saved by estimating, if possible, before beginning the operation, the approximate volume of standard solution which will be required for the titration. This makes it possible to run in rather rapidly almost the required amount, after which, of course, the end-point must be very carefully determined. In case such a calculation cannot be made, it is often worth while to ascertain this approximate volume by means of a very rapid preliminary titration: this of course will necessitate the use of an extra sample. (See, for example, the determination of manganese by titration with potassium permanganate.)

A. Neutralization Methods

alkalimetry and acidimetry

Standard solutions of acid and alkali are required for these processes, together with suitable indicators.

Standard Acid Solutions. These are generally prepared from hydrochloric or sulphuric acid. Hydrochloric acid has the advantage of forming soluble compounds with the alkali earths, but its solutions cannot be boiled without danger of loss. Both acids may be used with all indicators.

Standard Alkali Solutions. These may be prepared from sodium or potassium hydroxide, sodium carbonate, or barium hydroxide. Sodium and potassium hydroxides, if free from carbonate, may be used with all indicators, but they absorb carbon dioxide readily and attack the glass of bottles; sodium carbonate may be weighed directly for the preparation of standard solutions, provided its purity is assured, but with many indicators the liberation of carbonic acid is a disadvantage. Barium hydroxide solutions are free from carbon dioxide; if any of this gas is absorbed, it at once causes the formation of a precipitate. Barium hydroxide may be used with all indicators, but it is not freely soluble in water. In many cases in which it is desirable to have a more concentrated carbonate-free solution of alkali, a sodium hydroxide solution from which the carbonate has been removed by means of a slight excess of barium chloride is very serviceable. Carbonate-free solutions should be protected by means of a soda-lime absorption tube.

Half-normal or tenth-normal solutions are employed in most analyses, the latter strength being convenient when small amounts of acid or alkali are to be determined.

Indicators for Use in Alkalimetry and Acidimetry. The indicators used in these processes are organic substances, often of very complicated structure, each being capable of existence in two forms of different color, which are mutually transformable into one another at specific H^+- and OH^--ion concentrations.

An aqueous solution which is neutral contains H^+ and OH^- ions in equal concentration, and, so long as the solution is very dilute, the number of mols of water ionized in one liter is 0.0000001, or 10^{-7}, at 25°. Since in the ionization equilibrium, $H_2O \rightleftarrows H^+ + OH^-$, we must have $(H^+)(OH^-) = k$, it follows that in dilute solutions $(H^+)(OH^-) = 10^{-14}$.

If an acid is added to water, or to a dilute neutral solution, in sufficient amount to increase the H^+-ion concentration from 10^{-7} to 10^{-6}, then the OH^--ion concentration will fall to 10^{-8}. Only 0.0000009 mol of H^+ ion would be required to produce such a change in a liter of neutral solution, and this amount is contained in about 0.01 cc. of *tenth-normal* hydrochloric acid, while the addition of only 0.1 cc. to one liter would increase the H^+-ion concentration from 10^{-7} to 10^{-5}.

The color changes which are characteristic of these indicators do not as a rule occur in exactly neutral solutions. The accompanying table gives for some of the more common indicators, the H^+-ion concentrations at which the color changes occur.

It might seem, at first thought, that only an indicator which changes exactly at the neutral point would be suitable, but this is by no means true. In titrating a strong acid against a strong base a few hundredths of a cubic centimeter of tenth-normal acid or alkali in excess will carry the concentration of hydrogen or hydroxide ion so far to one side of the neutral point that any of the indicators for which the characteristic point lies between 10^{-5} and 10^{-9} will give a sharp and accurate end-point.

In titrating a weak acid with a strong base, *e.g.* acetic acid with sodium hydroxide, the acetate ions from the highly ionized sodium acetate drive the reaction, $HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$, far to the left, long before an equivalent quantity of the base has been added; the concentration of hydrogen ion becomes exceedingly low ($< 10^{-5}$ but $> 10^{-7}$) before the major portion of the acetic acid has had its hydrogen replaced. In such a case the change in color for *methyl orange* (see the Table) will appear gradually, during the addition of a cubic centimeter or more of

ACIDITY OF SOLUTIONS AT THE CHANGE OF COLOR FOR VARIOUS INDICATORS.

H+-ion Concentrate	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
Dimethylaminoazobenzene	Cherry Red	+	+	Flesh Colored	Golden Yellow	+	+	+	+	+					
Methyl Orange	Rose Red	+	+	+	Orange Red	Yellow	+	+	+	+					
Sodium Alizarinsulphonate	Greenish Yellow	+	+	+	+	+	Red	+	+	+	+				
Methyl Red			+	Red	+	Pink	Yellow	+	+						
Congo Red			+	Blue	Violet	Reddish Violet	Orange	Orange Red	+	+					
Cochineal			+	+	Yellow	Yellow Pink	Lilac	+	+	+					
Litmus			+	+	+	Red	Red Violet	Violet	Blue	+	+				
Rosolic Acid			+	Yellow	+	+	+	Rose	Red	+	+	+			
Guiac Tincture					Colorless	+	+	+	Greenish Yellow	+	+	+			
Phenolphthalein					+	Colorless	+	+	+	Red	+	+	+		
Thymolphthalein							Colorless	+	+	+	Blue	+	+	+	
Tropaolin O								Yellow	+	+	+	+	Orange Yellow	+	+
Trinitrobenzene										Colorless	+	+	+	Orange	+
Benzopurpurin											Yellow	+	+	+	Red

Taken in Modified Form from W. A. Noyes' "Textbook of Chemistry."

the alkali, long before an equivalent quantity of alkali has been run in, and no sharp end-point will be indicated. If *phenolphthalein* is used, however, the change in color will not occur until the true neutral point, $(H^+) = 10^{-7}$, has been passed; a very slight excess of alkali will then reduce the concentration of the hydrogen ion far below 10^{-8}, a sharp end-point will be indicated, and the total alkali added will correspond very exactly to that required for the actual neutralization of the acid.

When a weak base is titrated with a strong acid, *e.g.* ammonium hydroxide with hydrochloric acid, the conditions are reversed and such indicators as methyl orange, methyl red, or cochineal, which change color in a faintly acid solution (*i.e.* $H^+ > 10^{-7}$) are most suitable.

The following rules should be observed in the use of neutralization methods for the determination of acids and bases:

1. In the titration of a strong acid with a strong base, or *vice versa*, use any indicator in the list, from methyl orange to phenolphthalein.

2. In the titration of any acid other than a strong mineral acid with a strong base, use phenolphthalein, trinitrobenzene, or a similar indicator.

3. In the titration of a weak base with a strong acid, use methyl orange, Congo red, or a similar indicator.

4. Do not attempt to titrate a weak base against a weak acid.

The sensitivity of a given indicator may vary under widely differing conditions of temperature and dilution, and for that reason it is important to titrate approximately equal volumes of solution in standardization and in analysis; and when it is necessary, as is often the case, to titrate the solution at the boiling temperature, the standardization should take place under the same conditions. It is also obvious that since some acid or alkali is required to produce the change in the indicator itself, the amount of indicator used should be uniform and not excessive; usually three or four drops of the solution are ample.

Methyl orange solution is most readily prepared by dissolving 0.02–0.05 g. of the solid compound (also known as Orange III) in a very little alcohol and diluting with water to 100 cc. It may be successfully used for the titration of strong acids and bases, and is particularly useful in the determination of weak bases, such as ammonium hydroxide and certain weak organic bases. It can also be used in titrating with a strong acid the soluble salts of very weak acids, such as carbonates, sulphides, arsenites, borates, and silicates, because in such cases the acids which are liberated are too weak to affect the indicator, and the reddening of the solution does not take place until a very slight excess of the strong acid has been added. It should be used in *cold*, not too dilute solutions. Its sensitivity is less in the presence of large quantities of alkali salts, or of smaller quantities of certain other metallic salts.

Phenolphthalein solution is prepared by dissolving one gram of the solid compound in 100 cc. of alcohol. This indicator is particularly valuable in the determination of weak acids, especially of organic acids. It should not be used with ammonia or weaker bases. It is decolorized by carbonic acid, which must therefore be removed by heating when other substances are being determined; unlike methyl orange, it is sensitive in boiling-hot solutions. The volume of the solutions titrated should be approximately uniform in standardization and in analysis, and for the best results this volume should not in general exceed 125–150 cc.

THE PREPARATION AND STANDARDIZATION OF APPROXIMATELY HALF–NORMAL SOLUTIONS OF HYDROCHLORIC ACID AND SODIUM HYDROXIDE

Procedure. Pour into a 100-cc. measuring cylinder a volume of hydrochloric acid (sp. gr. 1.19, with 37.2% of HCl) sufficient to contain 36.5 g. of hydrogen chloride, transfer it quantitatively to a one-liter measuring flask, and dilute to the mark with distilled water. Pour this solution without loss into a clean, well-

drained 2½ liter bottle, refill the measuring flask with distilled water, and pour this also into the bottle. Finally shake the solution thoroughly for a full minute in the stoppered bottle, to insure uniformity of concentration.

Weigh out, upon a rough balance, about 42 g. of stick sodium hydroxide. Dissolve the alkali in water, in a large beaker, dilute this solution also to two liters, and shake for a full minute in the stoppered bottle.

Fill two clean, grease-free burettes with the respective solutions, first thoroughly rinsing each burette three times with 10 cc. portions of the corresponding solution and allowing the wash liquid each time to run out through the tip. See that all air bubbles are expelled from the tips, note the exact position of the liquid in each burette, and record the readings in the note-book. Run out from one burette about 20 cc. of the acid into a beaker, and add three drops of methyl orange solution; dilute the acid to about 80 cc., and run in alkali solution from the other burette, with stirring, until the color of the solution changes from pink to yellow. Wash down the sides of the beaker with a little distilled water, replace the beaker under the acid burette, and add acid to restore the pink; continue these alternations until the point is accurately fixed at which a single drop of either solution will produce a distinct change of color. Select as the end-point either the appearance of the faintest tinge of pink which can be recognized, or its disappearance, and always titrate to the same point. If the titration has occupied more than three minutes, the time required for draining, the readings of the burettes may be taken at once and entered in the notebook.

Refill the burettes and repeat the titration. Correct the burette readings as indicated by the burette calibrations, and if necessary for temperature (see Part I), and obtain the ratio of the solutions as shown in the following example:

$$\frac{\text{cc. acid}}{\text{cc. alkali}} = \frac{21.53}{21.07} = 1.022 \text{ cc. of acid per } 1.000 \text{ cc. of alkali.}$$

When this ratio has been satisfactorily established, the hydro-chloric acid solution is standardized as follows:

(*a*) *By Titration against Pure Sodium Carbonate.* If a suitable oven is available, dry the salt on a watch glass for an hour at 130–150°; otherwise heat about 5 g. of pure sodium carbonate in a small porcelain dish, on a wire gauze over a small Bunsen flame, for one half hour, and then allow the salt to cool in a desiccator. Transfer the cold salt to a dry, well-stoppered weighing tube, and weigh out into 400-cc. beakers two portions of 0.5–0.6 g. each,[1] noting the exact weights in the notebook. Pour over the salt about 80 cc. of water, stir until dissolved, and add three drops of methyl orange solution. Fill the burettes with the acid and alkali solutions, note the initial readings of the burettes, and run in the acid, with stirring, until the solution assumes the faintest tinge of pink. Wash down the sides of the beaker with a little water, and if the solution loses its pink tint add acid, one drop at a time, with stirring, until the faint pinkish tinge just returns. (If too much acid is added, the excess can be determined by means of the alkali in the other burette, since the ratio of the alkali to the acid is known.) After three minutes, note the burette readings and enter them in the notebook. From the data recorded, calculate the normality factor of the acid and also that of the alkali. The standardization of the acid must be repeated until the duplicate values agree within two parts in one thousand, and the same of course applies to the determination of the ratio of the two solutions.

(*b*) *Gravimetrically with Silver Nitrate.* Measure out accurately from a pipette 10.00 cc. of the acid into each of two 300-cc. beakers, and dilute in each case with 150 cc. of water. Precipitate the chlorine from these solutions with silver nitrate according to the procedure given in Part II, and filter the silver chloride off through Gooch crucibles, prepared and weighed as there indicated. Wash the precipitates with hot water until

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[1] The weights of samples in this book are based upon the use of 30-cc. burettes. If 50-cc. burettes are used, it is better to take samples ⅗ as large.

free from soluble silver salts, dry at 120–130° to constant weight, and from the weight of silver chloride found in each case calculate the normality factor of the acid. The duplicate values should agree very closely with one another, and also with those previously found by titration against sodium carbonate.

NOTES. — 1. Although silver chloride is insoluble, the normality factor of the hydrochloric acid may nevertheless be calculated directly from the weight of the precipitate obtained. For example, if 10.00 cc. of the acid were found to yield 0.7317 g. of AgCl, then (since an equal volume of normal HCl would yield 1.4334 g. of AgCl) the normality factor of the acid is 0.7317/1.4334, or 0.5105.

In the same way, the normality factor of the acid may be calculated in the case of Method (*a*). For example, if 0.5682 g. of Na_2CO_3 require 21.00 cc. of acid, the normality factor is equal to 0.5682/1.1130 = 0.5105 (1.1130 g. is the amount of Na_2CO_3 contained in 21.00 cc. of the normal solution).

If it has previously been found, for example, that 1.000 cc. of alkali solution is equivalent to 1.022 cc. of the acid, then it follows that the normality factor of the alkali is 0.5105 × 1.022 = 0.5217.

2. If it is desired to prepare solutions of exactly one half normal concentration, slightly stronger solutions are first prepared, and, after standardization, they are diluted with the calculated volume of water. For example, the 0.5105 *N* acid should be diluted according to the proportion, 0.5105 : 0.5000 = *x* : 1000, and the 0.5217 *N* alkali according to the proportion, 0.5217 : 0.5000 = *y* : 1000; *i.e.* one liter of each solution should have added to it 21.0 cc. and 43.2 cc. of water, respectively. The water is added from a burette. After dilution the solutions should be thoroughly shaken, and then restandardized.

3. Solutions should be thoroughly mixed to insure uniformity of concentration before standardization. They should be allowed to attain the temperature of the room, and they should be shaken to take up any water which may have evaporated and later condensed on the inner walls of the bottles. Before replacing the stopper in a bottle, always dry it, as well as the neck of the bottle, with a clean, lintless towel.

4. The liquid is diluted to 100 cc. during standardization in order that the volume may be the same as that which will prevail during analysis.

5. The exact point at which the color changes should be chosen as the end-point; any deeper tint is unsatisfactory, since it is not possible to duplicate shades of color from day to day by memory.

6. The selection of the best compound to be used as a standard for acid solutions has been the subject of much controversy. In many works calcium carbonate has been recommended (see Part IV, Problem 54), and also sodium carbonate, which can now be purchased sufficiently pure for this purpose. The most reliable standard would seem to be sodium carbonate prepared from recrystallized sodium bicarbonate by heating the latter between 280° and 300°. The bicarbonate is easily purified by crystallization, and between the temperatures named it is decomposed quantitatively according to the equation,

$$2 NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$
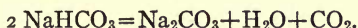
7. Instead of standardizing the acid solution, it is equally practicable to standardize the alkali solution, with the use of phenolphthalein, against any of the following pure acids: oxalic acid, $H_2C_2O_4 . 2 H_2O$; acid potassium oxalate, $KHC_2O_4 . H_2O$; potassium tetroxalate, $KH_3(C_2O_4)_2 . 2 H_2O$; potassium bitartrate, $KHC_4H_4O_6$; succinic acid, $H_2C_4H_4O_4$. The last two are probably the most suitable, since they are free from water of crystallization. It should be noted that the acid oxalate and the bitartrate contain one replaceable hydrogen atom each, while the tetroxalate contains three such atoms, and the oxalic and succinic acids two.

8. While it is permissible to standardize hydrochloric acid solutions (provided they are free from other chlorides) gravimetrically with silver nitrate, a solution of sulphuric acid should not be standardized in this way by precipitation as barium sulphate; the results would be less reliable on account of the difficulty in obtaining large precipitates of barium sulphate which are free from contamination and which are not partially reduced on ignition.

THE DETERMINATION OF THE TOTAL ALKALINE VALUE OF SODA ASH

The sample may be one of commercial soda ash, or it may be an artificial mixture of sodium carbonate and sodium chloride.

Procedure. Weigh out roughly on a watch glass 5 g. of the soda ash, and dry it for one hour at 110°; allow it to cool in a desiccator. Now accurately weigh the sample on the watch glass, transfer it quantitatively to a 500-cc. beaker, washing off the glass with about 50 cc. of water; dry and weigh the watch glass, and take the difference as the weight of the sample. Gently warm the sample with the 50 cc. of water and filter off any in-

I

soluble residue. Wash the filter at least five times with 20 cc. portions of warm water, and receive the filtrate and washings in a 250-cc. measuring flask which has been freed from grease by means of cold cleaning solution. Cool the liquid to the room temperature, add distilled water until the lowest point of the meniscus is level with the mark on the neck of the flask, and thoroughly mix the solution by pouring it from the flask into a dry beaker and back into the flask two or three times.

Measure off 25 cc. of the solution with a pipette (which should be previously rinsed out with small quantities of the solution) into a 300-cc. Erlenmeyer flask, allowing the pipette to drain for a second or two with the tip in contact with the inside wet surface of the flask (unless it was standardized otherwise). Dilute the solution to about 80 cc., add three drops of methyl orange solution, and titrate with the standard acid, using the standard alkali to complete the titration as already described. From the volumes of acid and alkali used, corrected for temperature difference and burette errors, calculate the percentage of alkali present, assuming the alkali to be wholly sodium carbonate.

Measure out other portions of 25 cc. from the main solution, and repeat the titration until satisfactory checks are obtained.

NOTES. — 1. Let us assume, for example, that 5.890 g. of soda ash were used in the preparation of 250.0 cc. of solution, and that 25.75 cc. of 0.5105 N acid and 4.13 cc. of 0.5217 N alkali were used in the titration of 25.00 cc. of this solution. Then it follows that 5.890 g. of the soda ash are equivalent to $10 \times (25.75 \times 0.5105 - 4.13 \times 0.5217) = 109.90$ cc. of N acid; and, since this volume of normal acid would neutralize an equal volume of normal alkali, therefore the 5.890 g. of soda ash contained $0.053 \times 109.90 = 5.8246$ g., or 98.9% of Na_2CO_3.

2. Soda ash is crude sodium carbonate. When made by the Solvay process it is apt to contain also sodium chloride, sulphate, and either the bicarbonate or hydroxide; if made by the Le Blanc process, which however has gone out of use, sodium sulphide, silicate, aluminate, and other impurities are likely to be present. Many of these contribute to the total alkaline value, but it is customary to calculate this value in terms of sodium carbonate alone.

3. In order to obtain uniform results, it is customary to dry the soda ash at 110° before analysis. Complete expulsion of the moisture would

require a very much higher temperature. At least 5 g. are taken, in order to secure a representative sample; but since this is too much for convenient titration, an aliquot portion of the solution is measured off.

4. For other methods of analyzing soda ash, the student should refer to Part IV, Problems 60, 61, and 95.

THE DETERMINATION OF THE NEUTRALIZATION VALUE OF AN ACID

Procedure. Weigh out accurately into 300-cc. beakers two 0.6–0.7 g. portions of the unknown acid (oxalic acid, acid potassium oxalate, potassium tetroxalate, potassium bitartrate, succinic acid, or some similar compound), dissolve each sample in about 80 cc. of warm water, add two or three drops of phenolphthalein solution, and run in half-normal alkali from a burette until the solution is pink. Add half-normal acid from the other burette until the pink color just disappears, and then exactly 0.30 cc. in excess. Heat the solution, and boil for three minutes. If the pink color reappears upon boiling, discharge it with acid, again add 0.30 cc. in excess, and repeat the boiling. Discharge the pink color if it again reappears, again adding 0.30 cc. in excess. Repeat this treatment until the pink color fails to return upon boiling for three minutes. Finally add alkali until the color just reappears, then *a drop or two* of acid in excess and boil for one minute. If no color appears during this time, complete the titration with alkali in the hot solution. From the corrected volume of alkali required to react with the acid solution, calculate the normality factor of a solution containing 10.00 g. of the unknown acid in one liter. The results should check within two parts in one thousand.

NOTES. — 1. Although it is desirable to employ the same indicator throughout standardization and analysis, the difference resulting from the change of indicator is in this instance insignificant, and the student may neglect it. It should be remembered, however, that in order to obtain the greatest accuracy possible, a restandardization throughout would be essential.

2. Since commercial sodium hydroxide always contains some carbonate, and since phenolphthalein is sensitive to carbonic acid, the solution must

I

be boiled to free it from this acid. Phenolphthalein does not show an alkaline reaction with cold dilute sodium bicarbonate solution; hence cold, dilute solutions of sodium carbonate become colorless with this indicator as soon as the carbonate has been transformed into bicarbonate by the acid. Upon boiling, the bicarbonate is partially hydrolyzed according to the equation, $Na^+HCO_3^- + H^+OH^- \lessgtr Na^+ + OH^- + H_2CO_3$, the solution loses carbon dioxide, and the pink color returns. This must again be discharged, the solution boiled, and so on.

3. Hydrochloric acid is volatilized from aqueous solutions upon boiling, unless they are *very* dilute. If the excess of acid added is not more than 0.30 cc., however, no loss need be feared.

4. When a large number of acidimetric determinations are to be made with phenolphthalein as the indicator, it is well worth while to prepare and standardize a carbonate-free alkali solution. The acid solutions are in such cases boiled, to free them from carbonic acid, or they are made up with freshly boiled water, and titrated hot with carbonate-free alkali (cf. the general discussion under alkalimetry and acidimetry).

THE DETERMINATION OF PROTEIN NITROGEN BY THE KJELDAHL METHOD

Principle. When an organic substance is heated with concentrated sulphuric acid, especially in the presence of an oxygen carrier, the organic substance is completely decomposed, and any protein (or other similarly combined) nitrogen is converted into ammonia. This at once combines with acid to form ammonium acid sulphate, NH_4HSO_4, which remains in solution in the sulphuric acid. Upon diluting the mixture with water and adding sodium hydroxide in excess, the ammonia is liberated, and can be distilled over and collected in a known volume of standard acid, which it partially neutralizes. By titrating the excess of acid with a standard alkali, the volume of the standard acid neutralized by the ammonia can be found, and from the data obtained the percentage of nitrogen in the sample may be calculated.

Procedure. Accurately weigh out from a weighing tube, upon separate sheets of quantitative filter paper, two samples of about 1 g. each of the substance to be analyzed. Wrap each

sample carefully in the paper, and introduce the bundle into a clean 500 cc. Kjeldahl flask. To each flask add about 0.5 g. of powdered copper sulphate, and 25 cc. of concentrated sulphuric acid. See that the samples are thoroughly wet by the acid, and then place the flasks on the digestion rack in the Nitrogen Laboratory, with the necks resting in the circular openings of the lead ventilating pipe; place the flasks in unoccupied positions as near as possible to one of the exhaust flues. Heat gently until frothing ceases, add 10 g. (weighed roughly) of potassium sulphate, or an equivalent weight of sodium sulphate, and heat to gentle ebullition for two or three hours until the liquid is of a clear green color, without any trace of brown (do not allow the flame to reach above the surface of the liquid). Continue the heating for half an hour longer, and allow to cool.

While the flasks are cooling, accurately measure from a burette two 30.00-cc. portions of 0.5 *N.* hydrochloric acid, into 400-cc. Erlenmeyer flasks, and add to each about 25 cc. of distilled water. Place these flasks under the distilling apparatus, so that the delivery tubes just dip into the acid solutions.

After cooling, carefully dilute the contents of the digestion flasks with 150 cc. of distilled water, and cool again. Carefully pour down the inclined neck of each flask, so that it shall not mix with the acid solution, 75 cc. of sodium hydroxide solution (300 g. of NaOH per liter). Place the flasks on the distilling rack, add one or two pieces of granulated zinc, and quickly connect the flasks with the distilling heads, using well-fitting rubber stoppers. Finally, mix the contents of each flask by gently rotating it, and then begin to heat the mixture.

Distill off about two thirds of the contents of each flask, with great care that they do not boil over. The distillation will require about 45 minutes. Disconnect the distilling flasks and rinse out the delivery tubes into the receiving flasks with a little distilled water. Add 3 drops of methyl orange to each of the receiving flasks, and titrate the contents with 0.5 *N.* sodium hydroxide.

From the data obtained, calculate the percentage of nitrogen in the sample.

NOTES. — 1. The sulphuric acid hydrolyzes the NH_2-group, to give ammonia, and also acts as an oxidizing agent, converting the organic matter into carbon dioxide, water, or other volatile products. For example, $CO(NH_2)_2 + H_2O + 2 H_2SO_4 = CO_2 + 2 NH_4HSO_4$; $C_6H_{10}O_5 + n H_2SO_4 = 6 C + 5 H_2O + n H_2SO_4$; and $C + 2 H_2SO_4 = CO_2 + 2 H_2O + 2 SO_2$.

2. The $CuSO_4$ gives up oxygen more readily to the organic matter than the H_2SO_4 does; but the H_2SO_4 then reoxidizes the copper so that at the end of the operation the copper is still present as copper sulphate. That is to say, the copper salt acts catalytically as an oxygen carrier.

3. Mercuric sulphate is often used instead of copper sulphate as an oxygen carrier, a few small globules of metallic mercury being added to the acid digestion mixture. Although the mercury salt is somewhat more efficient, it tenaciously retains ammonia, as $H_2N-Hg-O-SO_2-O-Hg-NH_2$, even in the presence of an excess of hot alkali, and it is therefore necessary to add also a large excess of sodium sulphide. This converts all the mercury into HgS, which combines with Na_2S to form soluble $Hg(SNa)_2$, and the ammonia is liberated.

4. The K_2SO_4 forms with the acid $KHSO_4$, and this serves to raise the boiling point of the sulphuric acid; the higher temperature hastens the digestion.

5. The flask is provided with a long neck in order that the acid fumes, which would otherwise be lost, may condense and run back into the digestion mixture.

6. After the acid solution has been diluted, it is specifically lighter than the NaOH solution used; upon pouring the latter carefully down the neck of the inclined flask, it sinks to the bottom and leaves the surface of the liquid still acid, thus preventing the loss of ammonia at this stage of the procedure. The contents should not be mixed until after the flask has been tightly connected with the distilling head.

7. The granulated zinc is added in order to prevent bumping during the distillation; the zinc dissolves slowly in the alkaline solution, with the evolution of hydrogen. Fragments of pumice stone or of platinum are often used for the same purpose.

8. If nitrates are present in the sample (*e.g.* a fertilizer), and it is desired to determine the total nitrogen, the procedure may be modified as follows: Thoroughly wet the sample in the flask with 25 cc. of concentrated sulphuric acid, in which one gram of salicylic acid $\left(C_6H_4\Big\langle{}^{OH}_{COOH}\right)$ has previ-

ously been dissolved; this reacts with the nitric acid to form nitrosalicylic acid, $C_6H_3 {-} OH {\diagup}^{NO_2}_{\diagdown COOH}$. Next add slowly, with frequent shaking, 10 g. of powdered sodium thiosulphate, which reduces the nitrosalicylic acid to aminosalicylic acid, $C_6H_3 {-} OH {\diagup}^{NH_2}_{\diagdown COOH}$. Now add 0.5 g. of powdered copper sulphate and complete the determination as already described, but omitting the addition of the alkali sulphate (the solution contains $NaHSO_4$ from the thiosulphate).

9. It is evident that ammonium salts may be analyzed for ammonia by simply distilling them with an excess of alkali, absorbing the ammonia in an excess of standard acid, etc. Moreover, nitric acid and nitrates may be quantitatively reduced to ammonia and determined in this way (see Part IV, Problems 63, 64, and 89).

Certain other salts, as acetates, may be analyzed in an analogous manner by distillation with phosphoric acid in excess, the distillate being collected in standard alkali and the excess of the latter titrated, with the use of phenolphthalein.

B. Methods of Oxidation and Reduction

In most oxidation and reduction processes the standard solution employed in the titration is one of an oxidizing agent, though it is often an advantage to have at hand a standard reducing solution as well. It may be stated, in general, that *oxidizable* substances are most often determined by direct titration, while *oxidizing* substances are very frequently determined by indirect titration (*i.e.* by adding the substance to an excess of reducing solution, and titrating either the excess of this solution or a product, as iodine, set free by the oxidizing substance).

Standard Solutions. The most important oxidizing agents employed in the form of standard solutions are potassium permanganate, potassium dichromate, iodine, potassium bromate, and ferric chloride; while the most important reducing agents are ferrous ammonium sulphate, oxalic acid, sodium thiosulphate, arsenious acid, and titanous chloride. Other oxidizing and reducing agents are frequently used in the processes, but not usually in the form of standard solutions.

The most important combinations among the foregoing standard solutions are: potassium permanganate and ferrous salts or oxalic acid; iodine and sodium thiosulphate or arsenious acid; potassium dichromate and ferrous salts.

Indicators. With respect to the indicators employed, potassium permanganate, owing to its own intense coloring power, is its own indicator; the slightest excess is indicated with great accuracy in otherwise colorless (or even in certain faintly colored) reaction mixtures. Since in the case of potassium dichromate no indicator has been found which is entirely satisfactory for use within the solution, potassium ferricyanide is employed as an outside indicator to determine the point at which the ferrous iron is completely oxidized. In the case of iodine, starch solution is employed as an indicator. The use of these indicators will be discussed under the respective processes.

1. DICHROMATE PROCESSES

Fundamental Principles. In the presence of hydrochloric or sulphuric acid, ferrous salts are promptly and completely oxidized in the cold to ferric salts upon the addition of potassium dichromate solution. Since hydrochloric acid is by far the most suitable solvent for iron and its compounds, the titration is most often carried out in the presence of this acid:

$$6\ FeCl_2 + K_2Cr_2O_7 + 14\ HCl = 6\ FeCl_3 + 2\ KCl + 2\ CrCl_3 + 7\ H_2O.$$
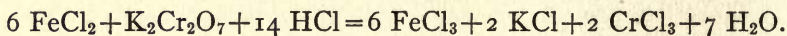
As an indicator, potassium ferricyanide is used outside the solution to determine the end-point of the reaction. A drop of the iron solution is added to one of the indicator solution on a white surface, and the mixture examined for a blue coloration due to the formation of insoluble ferrous ferricyanide. The potassium ferricyanide must of course be free from ferrocyanide, and the indicator solution must be very dilute to diminish the interference of its own color; a crystal the size of a pinhead dissolved in 25 cc. of water gives the right concentration. Since this solution is not stable, it must be freshly prepared each day.

THE PREPARATION AND STANDARDIZATION OF THE AP-PROXIMATELY TENTH-NORMAL DICHROMATE AND FERROUS IRON SOLUTIONS

Procedure. Pulverize about 3 g. of potassium dichromate, dissolve 2.5 g. of the powder in water, and dilute to 500 cc.; also dissolve 20 g. of ferrous ammonium sulphate and 5 g. of ammonium sulphate in water, with the addition of 5 cc. of concentrated sulphuric acid, and dilute to 500 cc. Thoroughly mix the solutions, see that they are of the room temperature, and then fill a burette with each solution, observing the precautions previously emphasized.

Prepare a solution of potassium ferricyanide of the strength recommended above, and place single drops of this solution on the surface of a white porcelain tile. Run out from a burette into a 300-cc. beaker about 20 cc. of the ferrous solution, add 15–20 cc. of 6-normal hydrochloric acid, dilute to 150 cc., and run in about 18 cc. of the dichromate solution from a second burette. Test at this point by adding a small drop of the well-mixed iron solution from the end of a stirring rod to a drop of indicator on the tile. (The stirring rod which has touched the indicator should be washed off with distilled water before being returned to the iron solution.) If a blue precipitate appears at once, 0.5 cc. of the dichromate solution may be added before another test is made. As soon as the blue appears to be less pronounced, add the dichromate solution in smaller amounts, finally a drop at a time, until the point is reached at which a bluish coloration fails to appear within 30 seconds after mixing a large drop of the iron solution with a drop of the indicator on the tile, the time being carefully noted. As soon as the 30 seconds have elapsed, remove another large drop of the iron solution and mix it with the indicator beside the last test; if no difference can be noted between the last mixture and this fresh one, the reaction is complete. Should the end-point accidentally be overstepped, more of the ferrous solution may be added and the titration pro-

ceeded with as before. Repeat this titration until good duplicates are obtained.

From the volumes of the solutions used (after applying any necessary corrections) calculate the value of the ferrous solution in terms of the dichromate solution; the ratios found should not differ by more than two parts in one thousand.

Standardize the dichromate solution as follows: Weigh out two portions of bright iron wire of about 0.15 g. each. The wire should be free from rust, and should be handled with filter paper. It should be bent so as not to interfere with the movement of the balance. Place 20-cc. portions of 6-normal hydrochloric acid in 300-cc. beakers, cover them with watch glasses, and heat to boiling. Remove the flames, drop in the portions of wire, and after the solution of the iron boil carefully for two or three minutes, keeping the beakers covered. Wash the sides of the beakers and the watch glasses with a *very little* water, and add stannous chloride solution to the *hot* liquid, drop by drop, until the mixture is colorless; avoid more than a drop or two in excess. Allow to cool, dilute with 150 cc. of cold water, and add rapidly with stirring 25 cc. of mercuric chloride solution. Allow the solutions to stand for two minutes, and titrate without further delay. (Calculate the volume of 0.1 N dichromate solution which would be required by the sample of wire, and add almost this quantity before beginning to test with the indicator.) The ferrous solution may be used if the end-point is passed.

From the volume of dichromate solution required to oxidize the known quantity of iron, calculate the normality factor of the solution. Repeat the standardization until duplicates are obtained which do not differ by more than two parts in a thousand, and from the mean of these calculate the normality factor of the ferrous ammonium sulphate solution.

NOTES. — 1. The ionic changes which occur during oxidation and reduction are more complicated than those of the methathetical reactions of precipitation and neutralization; in the case of oxidation and reduction

an ion may change its entire character. The electrical charges on the new ion may differ in sign as well as in number from those on the original ion. In equations expressing these ionic changes the algebraic sum of the charges is always the same on the two sides; in this case, for example, we have

$$6 \ Fe^{++} + Cr_2O_7^{--} + 14 \ H^+ = 6 \ Fe^{+++} + 2 \ Cr^{+++} + 7 \ H_2O.$$
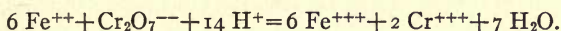
2. It is possible to prepare an exactly tenth-normal solution of the dichromate by dissolving 2.4517 g. of the pure salt in water and accurately diluting the solution to 500 cc. The commercial salt, however, should not be used for this purpose; it should be purified by recrystallization from hot water, and then dried at 130°.

3. The presence of ammonium sulphate and sulphuric acid in the ferrous ammonium sulphate seems to increase the stability of the ferrous solution.

4. The iron wire offered in the market for this purpose answers well as a standard, and the iron content of each lot purchased may be ascertained by a number of gravimetric determinations. It may be preserved in a desiccator over concentrated sulphuric acid, but this must not be allowed to come in contact with the wire; the wire should always be carefully examined for rust before use. If necessary, it should be cleaned with fine emery paper.

5. The solution of the wire in hot acid and the short boiling insure the removal of gaseous hydrocarbons, due to the presence in the iron of a small amount of carbon. If not expelled, these might reduce some of the dichromate solution. Their complete expulsion is even more important when the wire is used as a standard in connection with potassium permanganate.

6. In the determination of iron by this method it must be wholly present in the ferrous condition. The common agents for the reduction of ferric iron are stannous chloride, zinc, sulphurous acid, and hydrogen sulphide; of these stannous chloride is the most convenient, but it should be used in very slight excess. To this end, it should be added to the hot concentrated ferric solution. The removal of the small excess of stannous chloride is necessary, and this is readily accomplished by means of a large excess of mercuric chloride; the chlorides of mercury do not react with the iron salts nor with the dichromate under the analytical conditions. The reactions are, $2 \ FeCl_3 + SnCl_2 = 2 \ FeCl_2 + SnCl_4$; and $SnCl_2 + 2 \ HgCl_2 = SnCl_4 + Hg_2Cl_2$. The mercurous chloride is precipitated.

It is essential that stannous chloride should not be present in great excess and that the solution should be dilute and cold when the mercuric chloride is added; otherwise a secondary reaction is likely to take place with the reduction of mercurous chloride to metallic mercury ($SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2 \ Hg$), which would readily reduce the dichromate solution. The occurrence of this secondary reaction is indicated by the darkening of the

precipitate; in such a case the solution is worthless, and should be discarded. If the ferric solution is hot and concentrated upon the addition of the stannous chloride, the reduction takes place with the greatest ease and only a drop or two of the stannous solution in excess need be added.

7. The solution should be allowed to stand for a minute or two after the addition of the mercuric chloride, to permit the complete precipitation of the calomel. It should then be promptly titrated to avoid any reoxidation of the iron by the air.

8. Less than 30 seconds are required for the appearance of the reaction with the indicator when the ferrous iron has nearly all been oxidized; if the mixture is left too long, the combined effect of light and dust will lead to a partial reduction of the ferricyanide, with the formation of a blue precipitate of ferric ferrocyanide. Thirty seconds is a sufficient interval.

9. The accuracy of the titration may be impaired by the removal of too much of the solution for the tests; for that reason the tests should not be begun until most of the iron has been oxidized, but at the close of the titration drops of considerable size may properly be taken (see note concerning this point under the gravimetric determination of iron). It is best never to overstep the end-point. The stirring rod should be washed each time in order not to transfer any of the indicator to the main solution. If the end-point is determined as prescribed, the dichromate method is capable of giving very exact results.

THE DETERMINATION OF IRON IN SIDERITE

Procedure. Weigh out two portions of about 0.23–0.25 g. of the finely powdered ore into 300-cc. beakers, moisten the samples with water, cover the beakers, and add to each 20 cc. of 6-normal hydrochloric acid and about 0.2 g. of potassium chlorate. Heat at a temperature just below boiling until solvent action has ceased, and to the hot solution add stannous chloride solution, drop by drop, avoiding an excess greater than two drops. Add 150 cc. of cold water and 25 cc. of mercuric chloride solution, allow to stand for a minute, and proceed with the titration as already described. Finally, calculate the percentage of iron in the ore.

NOTES. — 1. Siderite is native ferrous carbonate; it may contain some organic matter, and, in order to destroy this, it is directed to add a little potassium chlorate to the hydrochloric acid.

2. Other ores can of course be analyzed by this method. Since most of them contain ferric iron, and since in the case of ferrous ores the iron is generally oxidized during the preparation of the solution, the quantity of stannous chloride required for the reduction of the iron will be much larger than that added to the solution of iron wire in the previous exercise. In no case, however, should stannous chloride solution be added in greater excess than two or three drops; otherwise it is apt to cause the separation of metallic mercury, and spoil the determination.

3. For another method of dissolving iron ores, see the determination of iron by means of potassium permanganate, and also Note 1 under that method.

THE DETERMINATION OF CHROMIUM IN CHROME IRON ORE

Procedure. Weigh out two portions of about 0.25 g. each into iron crucibles which have been scoured inside until bright. Weigh out upon watch glasses, on the rough laboratory balance, two 4-g. portions of dry sodium peroxide, pour about three quarters of each upon the samples of ore, and mix the ore and flux by means of a dry glass rod. Remove any adhering particles from the rod by stirring with it the remaining peroxide, and then pour the latter upon the surface of the mixture. (Owing to the tendency of the peroxide to absorb moisture, the first portion should be mixed with one sample before the second portion is weighed out from the container.) Place the crucible upon a triangle and raise the temperature very slowly to the melting point of the flux, using a low flame and holding the burner in the hand. Maintain the fusion for five minutes, stirring with a stout iron wire; do not heat above moderate redness.

Allow the crucible to cool until it can be held in the hand, and then cover it with water in a 300-cc. beaker, keeping the beaker covered with a watch glass. When the evolution of gas has ceased, rinse off and remove the crucible; heat the solution to boiling for 15 minutes in the covered beaker, add sufficient 6-normal sulphuric acid (calculated) to almost neutralize the liquid, and filter. To the filtrate and washings, which should

be slightly alkaline, add about 0.2 g. of sodium peroxide, boil for several minutes, acidify with 6-normal sulphuric acid, and add 10 cc. in excess.

Weigh out for each solution about 0.5 g. more than enough pure ferrous ammonium sulphate to reduce the chromate, on the assumption that the ore was pure chromite, $FeO . Cr_2O_3$. Dissolve the salt, in a 500-cc. Erlenmeyer flask, in about 50 cc. of freshly boiled water and 20 cc. of 6-normal sulphuric acid, and transfer to this flask the chromate solution, diluting the whole to about 200 cc. Promptly titrate the excess of ferrous iron with the standard dichromate solution.

From the data obtained, calculate the percentage of chromium in the ore.

NOTES. — 1. Chrome iron ore consists essentially of ferrous chromite, $Fe(CrO_2)_2$. The ore is decomposed by the flux, which oxidizes the iron oxide to sodium ferrate and dissolves and oxidizes the chromic oxide to sodium chromate:

$$2 FeO . Cr_2O_3 + 10 Na_2O_2 = 4 Na_2CrO_4 + 2 Na_2FeO_4 + 4 Na_2O.$$
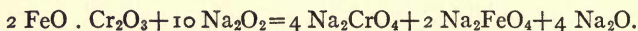
2. Fused sodium peroxide attacks most materials; although it attacks iron and nickel, crucibles of these metals may nevertheless be used if care is taken to keep the temperature as low as possible. The peroxide must be dry, and no dust or organic matter of any kind should be present; otherwise explosions may occur.

3. When iron crucibles are used, the fusion should be allowed to become cold before it is placed in water; otherwise magnetic oxide of iron, $FeO . Fe_2O_3$, is apt to scale off from the crucible. This will lead to no error, however, if the solution is only partially neutralized before filtration. Partial neutralization is to prevent the alkali from destroying the filter paper.

4. Upon treatment with water the chromate goes into solution, the sodium ferrate is decomposed into sodium hydroxide, ferric oxide, and oxygen, and the excess of sodium peroxide is decomposed with the evolution of oxygen. The subsequent boiling insures the complete decomposition of the peroxide, any of which if present would react with the chromate upon acidification. The alkaline chromate solution is always slightly reduced upon filtration through a paper filter; it is therefore directed to add to the filtrate a small quantity of sodium peroxide to reoxidize the chromium, and to boil a second time to destroy the excess.

5. The addition of acid transforms the sodium chromate into dichromate, which, of course, behaves like potassium dichromate in acid solution. If any of the sodium peroxide is allowed to remain undecomposed in the solution, the chromate is at least partially oxidized to a perchromate, upon acidification.

6. Instead of using $Fe(NH_4SO_4)_2 \cdot 6 H_2O$, the ferrous solution may be prepared from a suitable quantity of pure iron wire; or, of course, a standard ferrous ammonium sulphate solution itself may be added in excess. Perhaps an even better method for the determination of chromium consists in the addition of potassium iodide in excess to the acidified fusion extract, followed by the titration of the iodine with sodium thiosulphate solution:

$$Cr_2O_7^{--} + 6 I^- + 14 H^+ = 2 Cr^{+++} + 7 H_2O + 3 I_2;$$
and
$$2 Na_2S_2O_3 + I_2 = 2 NaI + Na_2S_4O_6.$$
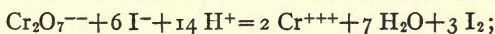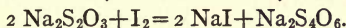
2. PERMANGANATE PROCESSES

Fundamental Principles. In acid solution, potassium permanganate promptly and completely oxidizes ferrous iron in the cold to ferric iron. Also, at 80–90°, it reacts quantitatively with oxalic acid, which it oxidizes to carbonic acid. Though in reality the reactions are not so simple, the quantitative relationships are accurately represented by the following equations:

$$10 FeSO_4 + 2 KMnO_4 + 9 H_2SO_4 = 5 Fe_2(SO_4)_3 + 2 KHSO_4$$
$$+ 2 MnSO_4 + 8 H_2O;$$
and
$$5 H_2C_2O_4 + 2 KMnO_4 + 4 H_2SO_4 = 2 KHSO_4 + 2 MnSO_4$$
$$+ 10 CO_2 + 8 H_2O.$$
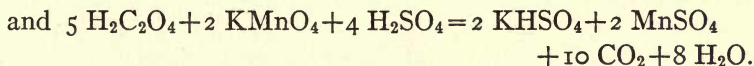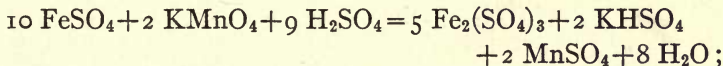
Or, more simply expressed,

$$5 Fe^{++} + MnO_4^- + 8 H^+ = 5 Fe^{+++} + Mn^{++} + 4 H_2O;$$
and
$$5 C_2O_4^{--} + 2 MnO_4^- + 16 H^+ = 2 Mn^{++} + 10 CO_2 + 8 H_2O.$$
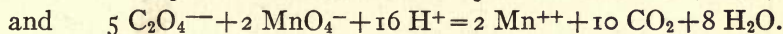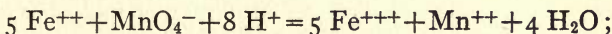
In a hot neutral or faintly acid solution, in the presence of zinc salts, potassium permanganate oxidizes manganous salts quantitatively in the sense of the equation,

$$3 Mn^{++} + 2 MnO_4^- + 2 H_2O = 4 H^+ + 5 MnO_2.$$
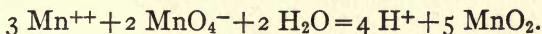
From these equations it is readily seen that for use in acid solution the normal weight of the salt is one fifth of a mol, or 31.61 g., while for use in neutral solution the normal weight is one third of a mol, or 52.68 g.

In addition to the above, potassium permanganate is capable of oxidizing stannous, cuprous, and mercurous salts, antimonious, arsenious, nitrous, and sulphurous acids, hydrogen sulphide, ferrocyanides, and many other substances.

Furthermore, as a less desirable feature, the permanganate is capable under certain conditions of oxidizing free hydrochloric acid, with the liberation of chlorine; the action is rapid in hot or strongly acid solutions, especially in the presence of ferrous iron, but slow in cold dilute solutions. It is possible, however, with suitable modifications, to obtain very exact results in the presence of hydrochloric acid, even in the titration of iron; but, other things being equal, in acid solution, it is preferable to carry out permanganate titrations in the absence of chlorides.

Potassium permanganate has an intense coloring power. Even the tenth-normal solution is so deeply colored that the lower line of the meniscus is not visible in an ordinary burette; readings must therefore be made from the upper edge. Moreover, the slightest excess added to an otherwise colorless solution is indicated with great accuracy; as its own indicator, it renders the titration one of the most satisfactory known.

The permanganate solution should not be placed in burettes with rubber tips; it is more or less rapidly reduced by most organic substances.

THE PREPARATION AND STANDARDIZATION OF AN AP-PROXIMATELY TENTH–NORMAL SOLUTION OF POTAS-SIUM PERMANGANATE

Procedure. Dissolve 3.25 g. of the permanganate crystals in 200 cc. of warm water, dilute the solution to one liter, and mix thoroughly. The value of this solution is apt to change slowly, especially just after it has been prepared. For this reason the solution should be allowed to stand for several days, and then filtered through a layer of asbestos to remove the precipitate of hydrated manganese dioxide. After thorough mixing, it is then ready for standardization. The solution should be pre-

served in glass-stoppered bottles, and should be protected from heat and light. Thus prepared and preserved, it will retain its oxidizing value for months. The solution is said to be still more stable if it is made very slightly alkaline with potassium hydroxide (before standardization, of course).

Weigh out accurately into 700 cc. Erlenmeyer flasks several 0.12–0.14 g. samples of pure sodium oxalate, previously dried at 110–120°; dissolve each sample in 250 cc. of hot water (80–90°), with the addition of 30 cc. of 6-normal sulphuric acid, and titrate at once with the permanganate solution. At first, the permanganate should be added drop by drop, with shaking after each addition until the color disappears. After several drops have been added, the solution may be run in slowly (10–12 cc. per minute) with continuous shaking. Toward the end of the titration, particular care must be taken to allow the color due to each drop to disappear before the addition of the next, in order to avoid passing the end-point. Titrate to the first permanent pink. The temperature at the end of the titration must not be below 60°.

From the data obtained, calculate the normality factor of the solution. Duplicate values should check within two parts in one thousand.

NOTES. — 1. It is not satisfactory to prepare a standard solution by directly weighing out the calculated quantity of potassium permanganate, even after the latter has been purified by recrystallization. The best practice is to prepare the solution as described in the procedure, and then to standardize it by comparison with iron wire or with sodium oxalate. Ferrous ammonium sulphate, oxalic acid, potassium tetroxalate, acid potassium oxalate, and other substances have been proposed as standards, but iron wire and sodium oxalate are readily obtainable in a sufficiently pure condition, and being non-hygroscopic and free from water of crystallization, their composition is less subject to change.

2. Upon treating a given weight of pure sodium oxalate with an excess of sulphuric acid, the corresponding weight of oxalic acid is set free; so that the use of this salt as a standard merely enables us easily to measure out a specific amount of oxalic acid. The oxidation of the oxalic acid by the permanganate is at first slow, and the permanganate should be added

K

dropwise, with full time for decolorization between successive drops. After a certain small amount of manganous sulphate has been produced in the solution, however, the speed of the reaction is very greatly increased (by the catalytic action of this substance) and the permanganate may be run in much faster.

THE DETERMINATION OF IRON IN HEMATITE

Principles. One of the most accurate methods for the determination of iron is based upon the oxidation of a chloride-free ferrous sulphate solution, in the presence of sulphuric acid, with potassium permanganate. Under these conditions, ferrous iron is oxidized and permanganate is reduced, according to the equation:

$$MnO_4^- + 5\ Fe^{++} + 8\ H^+ = Mn^{++} + 5\ Fe^{+++} + 4\ H_2O.$$
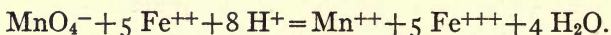
But if chlorides are present, some of the permanganate will be reduced by these, with the liberation (and partial escape) of chlorine, and the results will be somewhat high:

$$2\ MnO_4^- + 16\ H^+ + 10\ Cl^- = 2\ Mn^{++} + 8\ H_2O + 5\ Cl_2.$$
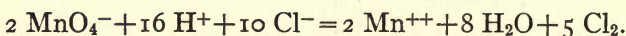
Upon the addition of the permanganate to a cold, dilute solution of hydrochloric acid alone, or to one containing ferric iron, no chlorine is evolved; ferrous iron, therefore, seems to accelerate this reaction by catalysis.

Nevertheless, since in dissolving iron ores it is nearly always necessary to use strong hydrochloric acid, to which it is often well to add a little stannous chloride, and since stannous chloride is a most convenient reagent for the reduction of ferric iron to the ferrous condition, it is desirable, if possible, to carry out the titration in the presence of fairly large quantities of chlorides.

Now it has been shown that if, when chlorides are present, a small quantity of manganous salt is added to the solution, the ferrous iron alone is oxidized, and that accurate titrations can be performed (Zimmermann). But the end-point is somewhat indistinct, owing to the yellow tint of the ferric chloride produced. This difficulty can be overcome by the addition of phosphoric and sulphuric acids (Reinhardt), which have recently

been shown to combine with ferric iron to form colorless complexes such as $H[Fe(SO_4)_2]$, $H_3[Fe(PO_4)_2]$, and $H_6[Fe(PO_4)_3]$ (Weinland and Ensgraber, *Zeitschrift für anorganische Chemie*, Vol. 84, p. 349); the large excesses of these acids repress the dissociation of these complexes and insure a colorless solution.

Procedure. Weigh out three samples of the finely ground ore, of about 0.25 g. each, into 100 cc. beakers. To each sample add 15 cc. of 6-normal hydrochloric acid and 2 cc. of stannous chloride solution, and gently heat the covered beakers for 10–15 minutes, until nothing other than a small, white, sandy residue remains undissolved. If the hot solution is at all yellow, discharge this color by adding stannous chloride solution, one drop at a time, with stirring; avoid an excess of more than two drops. If, however, after the heating, the solution is colorless, stannous chloride is present in unknown excess, and must be oxidized by adding permanganate solution (not to be counted, of course, in the volume required for the titration) drop by drop with stirring, until the yellow color due to ferric iron appears; discharge this color as above directed, with stannous chloride solution, one drop in excess.

After cooling, dilute the colorless solution with 50 cc. of cold water, and transfer, with stirring, to a 700-cc. beaker containing 10 cc. of mercuric chloride and 50 cc. of water. (If, instead of a white precipitate of calomel, a gray precipitate of mercury is formed at this point, the solution must be discarded.) Dilute the mixture with cold water to about 500 cc., add 8–10 cc. of the Zimmermann-Reinhardt solution,[1] and titrate at once with the standard permanganate solution. Add the permanganate slowly, with constant stirring, finally in single drops, until the pink color flashes throughout the solution and persists for 15–20 seconds; do not pass the end-point. Report the percentage of iron in the ore.

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[1] Made by dissolving 67 g. of $MnSO_4 \cdot 4 H_2O$ in 500 cc. of water, adding 138 cc. of phosphoric acid (sp. gr., 1.7) and 130 cc. of sulphuric acid (sp. gr., 1.84), and diluting with water to one liter.

NOTES. — 1. Many iron ores are not completely decomposed by hydrochloric acid, the insoluble residue containing more or less iron, as silicate, titaniferous iron, etc. Unless iron is known to be absent in the insoluble residue, the finely ground sample should be digested on the hot plate with 10 cc. of hydrochloric acid until the residue is white, or until there appears to be no further action; if the ore contains carbonaceous matter, a little potassium chlorate should be added. Finally evaporate to dryness, extract with 5 cc. of hydrochloric acid, dilute with 10 cc. of water, allow to settle, and decant the clear liquid through a small filter, transferring the residue to the filter and washing with as little cold water as possible. Ignite the filter and residue in a small platinum crucible, allow to cool, and add 20–30 drops of sulphuric acid and twice as much hydrofluoric acid. Heat carefully, and, if the residue is dissolved, evaporate to white fumes, allow to cool, dissolve in water, and add to the solution at first obtained. If, however, this treatment fails to decompose the residue, drive off most of the sulphuric acid, add 0.5–0.6 g. of potassium bisulphate, and heat gradually until the bisulphate is quite liquid and fumes of sulphuric acid are given off whenever the lid of the crucible is raised. When the black specks have disappeared, allow the crucible to cool and dissolve the salt in the crucible with hot water and a few drops of hydrochloric acid.

In case ferric iron has been dissolved in hydrochloric acid in contact with platinum, the solution should be oxidized with bromine water and the iron precipitated with ammonia; *i.e.* if it is desired to use stannous chloride in the reduction. The ferric hydroxide can then be redissolved (after washing it with hot water) in hydrochloric acid and reduced. Otherwise the iron solution will contain a small quantity of platinum, $4 FeCl_3 + 2 HCl + Pt = 4 FeCl_2 + H_2PtCl_6$, which gives a characteristic ferric-iron color with stannous chloride, and prevents the recognition of the point at which the iron is reduced.

2. Three samples should be taken, in order that one may be used for a rapid preliminary titration. Having ascertained in a rough manner the iron content of the sample, the final titrations are greatly facilitated.

3. Stannous chloride is a great help in the solution of many ores containing ferric iron. Apparently the difficultly soluble particles of hematite are continuously reduced at the surface to ferrous oxide, which is much more readily dissolved by the acid.

4. The available agents for the reduction of ferric iron are zinc, sulphurous acid, and hydrogen sulphide; stannous chloride is excluded unless the titration is to be made by the Zimmermann-Reinhardt method. In that case it should be carefully added, in very slight excess, to the hot, concentrated, acid solution (cf. the standardization of dichromate solution, Note 6).

5. Soluble salts of mercurous mercury are readily oxidized by potassium permanganate in acid solution. Mercurous chloride, however, is exceedingly insoluble, and, provided only a very small quantity is suspended in the solution, its action is so slow that the end-point of the titration can be accurately fixed. The pink color which flashes throughout the solution at the end of the titration is, however, not permanent, and for that reason the time-limit set should be closely observed. For the greatest accuracy, the permanganate should of course be standardized, under exactly the same conditions, against a known quantity of metallic iron. But the error due to the use of a solution standardized against sodium oxalate is for most purposes negligible.

6. For a rapid method for the reduction of ferric iron by means of zinc, see Notes 1 and 2 under the Determination of Phosphorus in Steel. It should be noted that titanium is also reduced by zinc, but not by the other agents mentioned; with the use of zinc, therefore the presence of titanium would lead to high results.

THE DETERMINATION OF CALCIUM IN LIMESTONE

Procedure. Instead of igniting the precipitate of calcium oxalate, obtained from the limestone by double precipitation according to the procedure described in Part II, and weighing it as calcium oxide, the calcium may be determined volumetrically as follows: Wash the reprecipitated calcium oxalate by decantation, keeping it as far as possible in the precipitation vessel, and decompose this precipitate by slowly pouring through the filter at least six 5-cc. portions of hot, 3-normal sulphuric acid, washing afterwards with hot water, and receiving the acid filtrate and washings in the beaker containing the bulk of the precipitate. Dilute this mixture to 100 cc. and warm gently, with stirring, to completely decompose the calcium oxalate. Allow the mixture to cool, transfer it quantitatively to a 250-cc. measuring flask, and dilute to the mark with water, finally mixing the solution by pouring it into a clean *dry* beaker and back into the flask.

Measure out by means of a pipette 50.00 cc. portions of this solution, add to each 30 cc. of 6-normal sulphuric acid, dilute to 300 cc., heat to 90°, and titrate as already described with the standard permanganate solution. Remembering that only one

fifth of the sample was used in each titration, calculate the percentage of CaO in the limestone.

NOTE. — The reactions involved in the volumetric determination of calcium are: $CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$; and $5 H_2C_2O_4 + 2 KMnO_4 + 4 H_2SO_4 = 2 KHSO_4 + 2 MnSO_4 + 10 CO_2 + 8 H_2O$. It is therefore plain that the normal or equivalent weight of calcium oxide in this case is one half of a mol, or that 0.1 N permanganate solution has a calcium oxide value of 0.00280 g. per cubic centimeter.

THE DETERMINATION OF THE OXIDIZING VALUE OF PYROLUSITE

Procedure. Weigh out two portions of the very finely ground mineral, of about 0.3 g. each, into 500 cc. Erlenmeyer flasks. Calculate the weight of ferrous ammonium sulphate, $Fe(NH_4SO_4)_2 . 6 H_2O$, required to react with each sample, assuming it to be pure manganese dioxide ($2 FeSO_4 + MnO_2 + 2 H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2 H_2O$), and weigh out accurately portions of the pure salt 0.15–0.20 g. in excess of the calculated amounts, into the corresponding flasks. Pour into each flask 50 cc. of water and 50 cc. of 6-normal sulphuric acid, cover the flasks, and heat to boiling until the action is complete. Finally, dilute to about 300 cc., and promptly titrate the excess of ferrous iron with the standard permanganate solution. From the data obtained, calculate the percentage of MnO_2 in the sample.

NOTES. — 1. The mineral should be so finely ground that no grit whatever can be detected when a little of the powder is placed between the teeth; upon this the success of the analysis largely depends. If properly ground, solution will be complete in 10–15 minutes.

2. A moderate excess of ferrous iron is necessary to promote rapid solution, and, also to facilitate solution, the mixture should not be diluted before the solvent action has ceased.

3. A solution of iron wire in sulphuric acid may be substituted for the ferrous ammonium sulphate, but in that case there is more danger of the partial oxidation of the iron by the air. For example, if iron wire is used, it should be dissolved in sulphuric acid out of contact with air, and the air should not have access to the solution during cooling. This is best accomplished by means of a Contat-Göckel valve, which consists of a glass

bulb with an inner siphon, as shown in the figure. In the bulb is placed a cold saturated solution of sodium bicarbonate, through which the hydrogen (and steam) evolved in the flask bubbles. After all the iron has been dissolved, the liquid is boiled for a few minutes longer, and the flame is removed. As the flask cools off, small portions of the bicarbonate are at intervals sucked into the flask and decomposed by the acid with the evolution of carbon dioxide, whereby the entrance of more bicarbonate solution is prevented.

For other methods of performing this analysis, see Part IV, Problems 23, 73 and 74. According to O. L. Barnebey (J. Ind. Eng. Chem., Vol. 9, p. 961 (1917)), the use of oxalic acid in place of the ferrous salt yields less reliable results.

4. With the substitution of very dilute nitric acid for sulphuric acid in the above procedure, the method may be used to determine the oxidizing power of red lead, or minium, Pb_3O_4, and of lead peroxide, PbO_2. Of these substances, samples of 1.0 and 0.8 g., respectively, should be taken when 30-cc. burettes are used. It is better, however, to make use of an iodometric method.
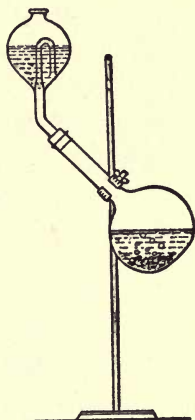
THE DETERMINATION OF PHOSPHORUS IN STEEL

Principle. The molybdic anhydride contained in ammonium phosphomolybdate, $(NH_4)_3PO_4 . 12 MoO_3$, may be reduced by zinc in the presence of sulphuric acid, from MoO_3 to Mo_2O_3; but molybdenum in the latter condition is not stable in the presence of air. If, however, the acidified molybdate solution is passed through a Jones reductor (see below) directly into a solution of ferric sulphate, the sensitive molybdic compound is oxidized by the ferric salt with the formation of an equivalent amount of ferrous sulphate, less sensitive to the atmospheric action. The molybdenum solution is green as it leaves the reductor, but upon mixing with the ferric salt the green color disappears; if phosphoric acid is added, the color due to the presence of ferric iron is destroyed. The decolorized solution is titrated while still hot with tenth-normal permanganate

solution, of which the quantity necessary corresponds to the equation,

$$5\ Mo_2O_3 + 6\ KMnO_4 = 3\ K_2O + 6\ MnO + 10\ MoO_3.$$
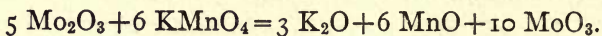
From this it may be seen that $5\ P \backsimeq 30\ Mo_2O_3 \backsimeq 36\ KMnO_4 \backsimeq 90\ O$, or $P \backsimeq 18\ O$; one cubic centimeter of $0.1\ N$ permanganate solution represents, therefore, 0.0862 mg. of phosphorus.

Procedure. Weigh out two samples of steel drillings, each sufficient to contain 1.7–2.0 mg. of phosphorus, into 250-cc. Erlenmeyer flasks. Add to each a mixture of 25 cc. of nitric acid (sp. gr., 1.42) and 75 cc. of water. Suspend in the neck of each flask a small funnel and heat until, after complete solution, the oxides of nitrogen have been expelled. Dissolve 0.3–0.4 g. of $KMnO_4$ crystals in 10 cc. of hot water, add one half of this solution to the contents of each flask, and boil until the permanganate color has disappeared. Remove the flame, add sulphurous acid or ammonium bisulphite solution, a few drops in excess, to dissolve the precipitated oxides of manganese, boil out the excess of sulphur dioxide, and filter the solution; receiving the filtrate in a similar flask. Add ammonia to the solution with stirring until a permanent precipitate just begins to form, and then add nitric acid drop by drop to clear up the solution. Finally, at a temperature of 40°, add 40 cc. of molybdate solution, close the flask with a rubber stopper, and shake vigorously for five minutes; allow the precipitate to settle. (At this point, prepare the Jones reductor for use, as described in Note 2.)

Now filter the solution, keeping the precipitate as far as possible in the flask, and wash by decantation with a solution of ammonium sulphate acidified with sulphuric acid [1] until the washings give no test for molybdenum with ammonium sulphide and hydrochloric acid. Dissolve the precipitate by pouring through the filter a mixture of 5 cc. of 6-normal ammonia and 20 cc. of water, and collecting the filtrate and washings in the

[1] Made by mixing 15 cc. of ammonia (sp. gr., 0.90) and 25 cc. of sulphuric acid (sp. gr., 1.84) with one liter of water.

precipitation flask. Acidify the solution, which should have a volume of about 60 cc., with 10 cc. of sulphuric acid (sp. gr., 1.84) and promptly pass the acidified solution, before it has a chance to cool off, through the reductor into the receiver (collecting the liquid beneath the surface of 100 cc. of a solution containing 25 g. of ferric alum and 40 cc. of sirupy phosphoric acid, sp. gr., 1.7, per liter), preceded by 100 cc. of hot water and followed by 200 cc. of hot dilute sulphuric acid (1 : 40) and 100 cc. of hot water. See that no air enters the reductor during this entire operation. Titrate the reduced solution at once with tenth-normal permanganate, and calculate the percentage of phosphorus in the steel on the assumption that the yellow precipitate contains phosphorus and molybdenum in the proportion indicated by the formula $(NH_4)_3PO_4 . 12 MoO_3$.

NOTES. — 1. The Jones reductor, which also is useful in the reduction of ferric iron for titration, is essentially a column of amalgamated zinc, through which the solution is passed for reduction. It is assembled as shown in the accompanying figure. The tube A has an inside diameter of about 18 mm. and (for this reduction) is 400 mm. long; the small extension tube has an inside diameter of 6 mm. and a length of 300 mm. below the stopcock. At the base of the tube A are placed some glass beads; these are covered by a plug of glass wool several millimeters thick, and upon this is placed a layer of asbestos, such as is used for Gooch filters, not exceeding 1 mm. in thickness. The tube is then filled with the amalgamated zinc to within 50 mm. of the top, and this is covered with a plug of glass wool. The reductor is connected as shown with the suction bottle F, and the bottle D is a safety vessel to prevent contamination of the solution from the suction apparatus.
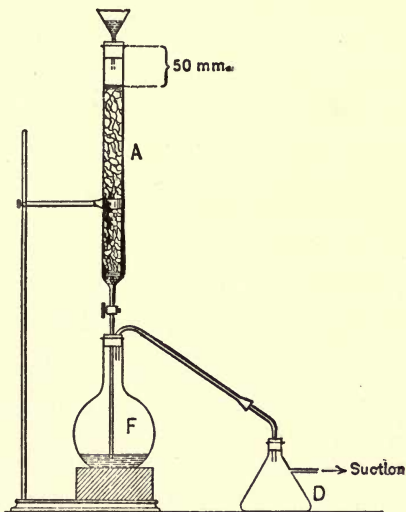
The amalgamated zinc is prepared by dissolving 5–6 g. of mercuric chloride in 250 cc. of water, with the addition of 5–10 cc. of dilute hydrochloric acid, adding to this solution 500 g. of (20–30 mesh) granulated zinc, in a large flask, and shaking thoroughly for two minutes; the solution is then poured off and the zinc thoroughly washed with water.

2. To prepare the reductor for use, connect the safety bottle with the vacuum pump, fill the reductor while the stopcock is nearly closed with warm, dilute sulphuric acid (25 cc. of the concentrated acid in one liter), and then open the stopcock so that the acid runs through slowly. Continue to pour in acid until 200–300 cc. have passed through, then close the cock *while some liquid is still left in the funnel.* (During the whole operation, see that no air enters the reductor; if air enters, hydrogen peroxide will be formed from oxygen and nascent hydrogen, and the results will be worthless.) Now remove the filtrate, and again pass through 200 cc. of the warm acid, followed by 100 cc. of warm water; test this liquid (300 cc.) with the standard permanganate solution, in order to determine the volume of permanganate required to color the acid alone. This amount must be subtracted from the volume required in the subsequent titration.

3. Upon dissolving the steel in nitric acid of the strength indicated, the phosphorus is oxidized, and none of it is lost by evolution as phosphine. The permanganate is subsequently added in order to insure the complete oxidation of carbonaceous matter and of the phosphorus to phosphoric acid.

4. The higher oxides of manganese, as MnO_2, are not soluble in nitric acid. Upon the addition of a reducing agent, however, such as hydrogen peroxide or sulphurous acid, their solution is effected:

$$MnO_2 + H_2SO_3 = MnO + H_2SO_4 = MnSO_4 + H_2O.$$
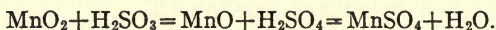
5. In connection with the precipitation of phosphoric acid as ammonium phosphomolybdate, the student should consult the notes under the Determination of Phosphoric Anhydride.

6. Since the molybdenum in the precipitate prepared from one gram of a steel containing 0.15% of phosphorus would require by this method 17.44 cc. of 0.1-normal permanganate solution, it is readily seen that the process is a rapid one for arriving at very accurate results. This is especially true if the permanganate has been standardized under the same conditions against a steel of accurately known phosphorus content; in such a case, it would be unnecessary to correct for the small amount of iron extracted from the (impure) amalgamated zinc, since this would be the same in both standardization and analysis.

7. It scarcely needs to be pointed out that the method is not suitable for determining phosphorus or phosphoric acid in substances containing them

in large amount. This would require for titration relatively enormous quantities of permanganate solution, and, what is still worse, it would be practically impossible to completely reduce the molybdenum. If small aliquot portions were taken for reduction and titration, any error of measurement would be multiplied by a very large factor in the calculation of the result.

8. The following method is suitable for the volumetric determination of phosphorus or phosphoric acid when these are present in larger amounts. The phosphorus or phosphoric acid is converted into ammonium phosphomolybdate; this, after washing with KNO_3 solution, is dissolved in an excess of standard sodium hydroxide solution; and the resulting solution is titrated with standard nitric acid, with phenolphthalein as an indicator. Needless to say, the sodium hydroxide should be standardized under identical conditions against a sample of accurately known phosphorus content.

THE DETERMINATION OF MANGANESE IN AN ORE

Fundamental Principles. When potassium permanganate is added to a hot, neutral or very faintly acid solution of manganese sulphate a reaction takes place (*the Guyard reaction*) in which the manganous oxide of the sulphate is oxidized at the expense of the anhydride of the permanganate, with the precipitation of hydrated intermediate oxides *in varying proportions*. These are manganous acid, $MnO(OH)_2$, and hydrated salts of manganous acid. The essential changes in the state of oxidation may be represented as follows:

$$Mn_2O_7 + 3\ MnO = 5\ MnO_2\ ;$$
$$Mn_2O_7 + 8\ MnO = 5(MnO_2 \cdot MnO)\ ;$$
$$Mn_2O_7 + 13\ MnO = 5(MnO_2 \cdot 2\ MnO).$$
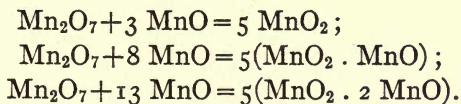
It is clear, then, that in this form the Guyard reaction cannot furnish the basis for a satisfactory volumetric method.

It has been found, however, that under suitable conditions, in the presence of zinc ion, a hydrated manganite of zinc is precipitated, which, while variable in composition, *contains all the manganese in the quadrivalent condition*. Thus regulated, the reaction furnishes a valuable means for the determination of manganese (Volhard's Method). Although the composition of

the precipitate varies, the course of the reaction is typically represented by the following equation:

$$4\,KMnO_4 + 5\,ZnSO_4 + 6\,MnSO_4 + 14\,H_2O = 2\,K_2SO_4 + 9\,H_2SO_4$$
$$+ 5\,Zn\left(OMn\underset{O}{\overset{OH}{\lessgtr}}\right)_2,$$

or, more simply,

$$2\,MnO_4^- + 3\,Mn^{++} + 2\,H_2O = 4\,H^+ + 5\,MnO_2.$$
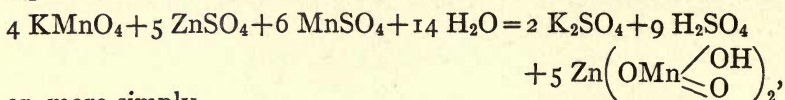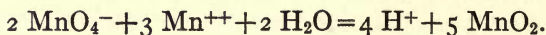
Procedure. Weigh out into a 500-cc. Erlenmeyer flask a sufficient quantity of the very finely ground ore to contain about 0.20 g. of manganese; add 3 g. of potassium chlorate and 20 cc. of 12-normal hydrochloric acid, and boil until the ore is completely decomposed and the chlorine expelled. Dilute with water to about 50 cc.; transfer the cold solution quantitatively to a 100-cc. measuring flask; dilute to the mark with water; and mix thoroughly by pouring the contents of the flask into a clean, dry beaker, and back into the flask.

Now, from a burette or pipette, measure into 500-cc. Erlenmeyer flasks four 20.00 cc. portions of this solution, and treat each as follows: Dilute with water to 100 cc., heat, and to the acid solution add with shaking an aqueous suspension of zinc oxide,[1] in small portions, until the iron is completely precipitated as ferric hydroxide; this point may be recognized by the sudden coagulation of the precipitate, upon shaking, and the decolorization of the brownish colored solution. The precipitate should not be light yellow, but should have the characteristic brownish red color of ferric hydroxide, and the least possible excess of zinc oxide should be used. (Should the ore contain a quantity

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[1] Dissolve 100 g. of crystallized zinc sulphate in 300 cc. of hot water, and with stirring cautiously add to the clear solution a few drops of a solution made by dissolving 25–27 g. of pure sodium hydroxide in 150 cc. of water, until the zinc solution remains distinctly turbid; then add a little bromine water, heat, and filter. To the filtrate add the bulk of the sodium hydroxide solution, and stir. Rinse the mixture into a one-liter bottle, and fill the latter with water. The mixture should be well shaken when used. (This suspension should not react alkaline with phenolphthalein, and a 10 cc. portion of the mixture, when cleared up with sulphuric acid, diluted to 100 cc., and treated with one drop of 0.1 N KMnO$_4$, should be permanently colored pink.)

of iron insufficiently in excess of that required by any phosphoric and arsenic acids present, then 5 cc. of a solution containing 20 g. of ferric chloride per liter should be added before the precipitation with zinc oxide.) If too much zinc oxide is added, the solution will be milky; in that case very dilute hydrochloric acid should be added drop by drop to the hot solution until the supernatant liquid just becomes clear.

Finally dilute the solutions to 300 cc. and, at 80°, treat them successively as follows: Run into the first solution the standard permanganate in 5 cc. portions, until after continued shaking the liquid retains a permanent pink tinge, — say after the addition of the fifth portion (*i.e.* 25 cc.); into the second solution run 5 cc. less permanganate than the volume previously used (*e.g.* 20 cc.), shake until the pink color disappears, and then finish the titration by the further addition of permanganate in portions of 1 cc. until the pink color persists after protracted shaking, say after 23.0 cc. in all have been added; to the third solution add at once 1.0 cc. less permanganate than the total volume used in the second case (*e.g.* 22.0 cc.), and continue the titration with the addition of 0.20 cc. portions, until the hot solution matches in color a solution prepared by the addition of 0.10 cc. of the permanganate to 300 cc. of water. With the fourth solution, repeat this titration. If, for example, 22.60 cc. of the permanganate have been used in each of the last two titrations, then this quantity minus the 0.10 cc. of the solution used for comparison should be taken as the volume actually required. Report the percentage of manganese in the ore.

NOTES. — 1. In case the treatment with hydrochloric acid and potassium chlorate should be insufficient to thoroughly decompose the ore (indicated by the presence of a dark-colored residue), the residue should be filtered off, washed, dried, and ignited in a platinum crucible. It should then be fused with sodium carbonate, the melt dissolved in hydrochloric acid, and the solution evaporated to dryness in a porcelain dish, to dehydrate the silica. The final residue should be moistened with hydrochloric acid, taken up in water, and filtered into the Erlenmeyer flask containing the acid filtrate from the original residue. The resulting solution, which

contains all the manganese, is then evaporated to a small volume, transferred to the measuring flask, and treated as described in the procedure.

2. Upon the addition of zinc oxide to the acid solution of the ore, the zinc oxide first neutralizes the acid with the formation of zinc chloride, and then precipitates the iron with the further formation of zinc chloride, according to the reaction: $2 FeCl_3 + 3 ZnO + 3 H_2O = 2 Fe(OH)_3 + 3 ZnCl_2$. In this way sufficient zinc ion is introduced into the solution to insure the conversion of the manganese into the hydrated manganite of zinc.

3. Although it is often recommended to convert the chlorides in the solution into sulphates before the addition of zinc oxide, this treatment is not necessary. The titration of manganese in a dilute neutral solution with potassium permanganate is a very different thing from that of *ferrous iron* in a dilute *acid* solution containing chlorides. In the latter case, the ferrous iron catalyzes the reaction, $2 KMnO_4 + 16 HCl = 2 KCl + 2 MnCl_2 + 5 Cl_2 + 8 H_2O$, some of the chlorine escapes, and there is a tendency to high results. In the former case, however, nothing is present in the solution to catalyze the reaction between the permanganate and the small quantity of hydrochloric acid which is formed; and, although the solution is hot, its acid concentration is so low that there is no danger from this source. Starting with 0.2000 g. of an ore containing 20% of manganese, for example, the total quantity of acid formed in the titration (*e.g* $4 KMnO_4 + 5 ZnCl_2 + 6 MnCl_2 + 14 H_2O = 4 KCl + 18 HCl + 5 ZnO . Mn_2O_3(OH)_2$) weighs about $\frac{3 HCl}{Mn} \times 0.04$, or somewhat less than 0.1 g.; and this quantity in a volume of over 300 cc. would give an acid strength of less than 0.01-normal.

4. The titration should be performed at 80–85°, and especial care should be taken not to heat the solution too hot during the titration.

5. For the greatest accuracy, in spite of all that has been said above, the permanganate solution should be standardized against a known quantity of manganese, weighed as $MnSO_4$, under conditions similar to those to be used in the analysis.

3. IODOMETRIC PROCESSES

Fundamental Considerations. Analytical processes which depend upon the volumetric measurement of specific amounts of iodine are known as *iodometric methods*. In these processes, either iodine is used in standard solution to bring about a definite reaction, or the iodine liberated in a reaction is determined by titration with some suitable standardized reagent.

The titration of iodine against sodium thiosulphate, with starch as an indicator, is one of the most accurate of volumetric processes. The process may be used in neutral or slightly acid solutions to determine free iodine, and this in turn may serve as a measure of any substance capable of liberating iodine from hydriodic acid. For example, the quantity of potassium iodate in a sample of the salt may be determined on the basis of the reactions:

$$KIO_3 + 6\ KI + 6\ HCl = 6\ KCl + KI + 3\ I_2 + 3\ H_2O\ ;$$
and $$I_2 + 2\ Na_2S_2O_3 = 2\ NaI + Na_2S_4O_6.$$
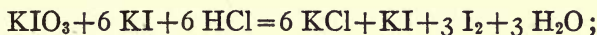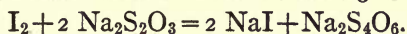
It should be noted that chlorine and bromine oxidize sodium thiosulphate partially to sulphate, while, under analytical conditions, iodine oxidizes it wholly to sodium tetrathionate.

Iodine acts as an oxidizing agent either through the direct withdrawal of a positive constituent, as shown in the equations: $2\ Na_2S_2O_3 + I_2 = 2\ NaI + Na_2S_4O_6$, and $H_2S + I_2 = 2\ HI + S$, or through the decomposition of water in the presence of a reducing agent, as in the equations: $H_2SO_3 + I_2 + H_2O \rightleftarrows H_2SO_4 + 2\ HI$, and $H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2\ HI$ ($H_2O + I_2 \rightleftarrows HI + HOI$; and $H_3AsO_3 + HOI \rightleftarrows H_3AsO_4 + HI$). It will be seen from these equations that a one-tenth normal iodine solution contains one tenth of one gram-atom, or 12.692 g. of iodine per liter.

The solubility of iodine in water is too small for the preparation of even a one-tenth normal solution. In the presence of sufficient potassium iodide, however, the iodine dissolves much more readily, owing to the formation of an unstable but soluble polyiodide of the formula KI_3:

$$KI + I_2 \rightleftarrows KI \cdot I_2,\ \text{or}\ I^- + I_2 \rightleftarrows (I \cdot I_2)^-.$$
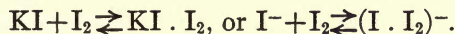
In the presence of reducing agents iodine is removed from this equilibrium mixture, the reaction runs to completion from right to left, and the solution can be used as though it were a simple solution of iodine. The potassium iodide used in the preparation of the solution should weigh about 1.5 times as much as

the iodine. Moreover, the presence of potassium iodide in the solution renders it possible to employ commercial iodine (which is apt to contain chlorine as an impurity) in the preparation of the standard solutions; the chlorine is removed according to the equation, $ICl + KI = KCl + I_2$.

In performing iodometric titrations in the presence of sulphuric acid, particular attention should be given to the maintenance of suitable analytical conditions. If, for example, it is desired to determine copper by titrating the iodine liberated in the reaction, $2 \ CuSO_4 + 2 \ H_2SO_4 + 4 \ KI \leftrightarrows Cu_2I_2 + 4 \ KHSO_4 + I_2$, it is not sufficient to simply add potassium iodide and sulphuric acid in (unknown) excess. It must be remembered that such a mixture will contain both sulphuric and hydriodic acid, and that if the concentration of either is too great, or if the solution is allowed to become at all warm, the determination is very apt to be spoiled: $H_2SO_4 + 2 \ HI = H_2SO_3 + H_2O + I_2$; $H_2SO_4 + 6 \ HI = S + 4 \ H_2O + 3 \ I_2$; or, in extreme cases, $H_2SO_4 + 8 \ HI = H_2S + 4 \ H_2O + 4 \ I_2$. Other things being equal, when acid solutions are required, it is better to use acetic acid or dilute hydrochloric acid.

In direct titrations with iodine, *e.g.* in the presence of sodium bicarbonate, it is best to work in the absence of ammonium salts. Such solutions are very faintly alkaline, especially if at all warm; and in the presence of ammonium salts ammonia is apt to be liberated, which is not entirely without influence upon the titration.

Iodine solutions act upon rubber, so that burettes with glass stopcocks should be used.

Determination of the End-point. A single drop of one-tenth normal iodine solution imparts a distinct tint to 200 cc. of water, and in many titrations with this solution no other indicator is required. If, however, the solution to be titrated contains colored substances, or if the greatest possible accuracy is demanded, a solution of starch should be used as an indicator. Under the proper conditions, the presence of one part of free iodine in

several millions of solution can be recognized with this indicator, but the sensitiveness of the reaction and the color produced are affected by a number of factors. The test is decidedly more sentitive when the concentration of iodide ion (and of hydrogen ion [1]) is not too low, and when the quantity of starch present is sufficient to give a deep blue color.

Under less favorable conditions, the starch may give a greenish or a reddish color; or it may be very unreliable, as in solutions containing an abnormally low iodide ion concentration. However, since the standard iodine solution always contains potassium iodide, and since an iodide is always one product of the titration, there is ordinarily not much danger from this source. Attention should be directed mainly toward the observance of uniform conditions in all related titrations: the volumes of the solutions titrated should be approximately equal, the starch solution should be properly prepared, and the same quantity of it should be added for each titration. Finally, all titrations should be made in the cold; the iodo-starch blue is discharged by heat.

Preparation of the Starch Solution. Rub 1 g. of potato starch with 5 cc. of cold water to a smooth paste, and slowly add this to 200 cc. of boiling water. Continue the boiling for about 1 min. until an almost clear solution is obtained, set this aside to settle, and finally decant the supernatant liquid through a filter. Use 5 cc. of the clear filtrate for each titration.

A " soluble starch " which is in the market is more convenient, since with it filtration is unnecessary. A solution made by adding 200 cc. of boiling water to 1.0 g. of this starch, previously mixed with a little cold water, serves the purpose well. Use 5 cc. of this solution for each titration.

In either case, the starch solution should be freshly prepared. If a great many titrations are to be made, however, it is advisable to prepare a liter of the starch solution; a number of

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[1] The iodo-starch blue is discharged by caustic alkalies and somewhat less readily by sodium or potassium carbonate, but not by the bicarbonates.

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small (50–100 cc.) bottles should be filled with this solution, heated for two hours in a water bath, and, while still in the bath, they should be closed with paraffined soft cork stoppers. Thus sterilized and protected from the air, the solution will retain its sensitiveness almost indefinitely. After a bottle has been opened, mould nearly always begins to form within a few days; hence the use of small bottles.

THE PREPARATION AND STANDARDIZATION OF APPROXIMATELY ONE–TENTH NORMAL SOLUTIONS OF IODINE AND SODIUM THIOSULPHATE

Procedure. Weigh out on the rough laboratory balance 6.3–6.4 g. of commercial iodine, add it to a solution of 9 g. of potassium iodide in 25 cc. of water, in an Erlenmeyer flask, and agitate the mixture until the iodine is completely dissolved. Dilute the solution to 500 cc., in a measuring flask, and mix it thoroughly.

Heat 600–700 cc. of distilled water in a large flask and boil for about 5 minutes. Stopper the flask loosely, and allow the water to cool. Weigh out 12.5 g. of sodium thiosulphate, $Na_2S_2O_3 . 5 H_2O$, introduce it into a 500-cc. measuring flask, and dissolve it in about 200 cc. of the cold, freshly boiled water. Finally dilute to the mark with more of the same water, and mix thoroughly.

After these solutions have come to the room temperature, fill a burette with each (the iodine in a glass-stoppered burette), observing the usual precautions to prevent dilution. Run out 25 cc. of the thiosulphate solution into a beaker, dilute with 150 cc. of water, add 5 cc. of starch solution, and titrate with the iodine to the appearance of the blue of the iodo-starch. If the end-point is overstepped, titrate back with the thiosulphate solution. (*All waste solutions containing iodine and potassium iodide should be poured into the vessel provided for iodine residues.*) Repeat until the ratio of the two solutions is accurately established, taking into account all necessary corrections for burettes and for temperature changes.

Standardization of the Iodine Solution. Weigh out into 500-cc. beakers two 0.12–0.13-g. portions of pure arsenious oxide, and in each case dissolve the arsenious oxide in 10 cc. of 6-normal sodium hydroxide solution. Dilute the solution to 100 cc., add 2 drops of methyl orange, and then cautiously add 6-normal hydrochloric acid until the solution contains 2 or 3 drops in excess. Cover the beakers, add to each a solution of 5 g. of pure sodium bicarbonate in 75 cc. of cold water, then add 5 cc. of starch solution, and titrate with the iodine to the appearance of the blue color. Do not pass the end-point. From the corrected volume of the iodine solution used, calculate the normality factor of the solution. Duplicate values should agree within two parts in one thousand. Also, from the ratio previously found, calculate the normality factor of the thiosulphate solution.

NOTES. — 1. Iodine solutions are acted upon by sunlight with the formation of hydriodic acid, and a high room-temperature tends to volatilize the iodine. They require frequent standardization against pure arsenious acid, anhydrous sodium thiosulphate, or standard thiosulphate solution.

2. Sodium thiosulphate, $Na_2S_2O_3 . 5 H_2O$, may be obtained pure by recrystallization. It is then possible to prepare a standard solution by dissolving the calculated weight of the salt in pure cold water, and dilution to the required volume. Such solutions are quite stable and may be kept for months without appreciable change in concentration, provided they are not allowed to absorb carbon dioxide; but they should be protected from heat and light, both of which are likely to promote decomposition.

3. Carbonic acid causes a slow decomposition of the thiosulphate solution, with the formation of free sulphur and sulphurous acid; and, since sulphurous acid acts in the same way, the decomposition once started becomes progressive:

$$Na_2S_2O_3 + H_2CO_3 \rightleftarrows \begin{cases} Na_2CO_3 + \\ H_2S_2O_3 \end{cases} \rightleftarrows H_2SO_3 + S,$$

and

$$Na_2S_2O_3 + H_2SO_3 \rightleftarrows \begin{cases} Na_2SO_3 + \\ H_2S_2O_3 \end{cases} \rightleftarrows H_2SO_3 + S.$$
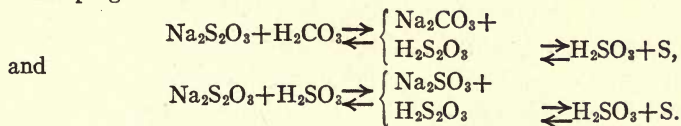
The reducing value of the solution increases gradually as the decomposition progresses; *i.e.* the solution apparently becomes stronger. When it is considered that in this decomposition each molecule of thiosulphate yields one

molecule of sulphite, the greater reducing value is readily understood; for $2 Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2 NaI$, while $1 Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2 HI$.

4. Solutions of the thiosulphate may be standardized against pure iodine, or, more conveniently (with the help of pure potassium iodide), against potassium bromate, potassium iodate, or potassium dichromate. These three salts are readily obtainable in a pure condition.

5. Arsenious oxide dissolves most readily in caustic alkalies, and for this reason the sodium hydroxide is used. The presence of sodium hydroxide is not admissible, however, during the titration, since it reacts readily with iodine. It is therefore removed by the addition of a slight excess of acid, and sodium bicarbonate is then added in large excess. The purpose of the bicarbonate, which under the analytical conditions is without action upon the iodine, is to neutralize the acid formed in the reversible reaction, $As_2O_3 + 2 I_2 + 2 H_2O \rightleftarrows As_2O_5 + 4 HI$, and thus cause it to run to completion from left to right. The reaction may then be written:

$$Na_2HAsO_3 + I_2 + 2 NaHCO_3 = Na_2HAsO_4 + 2 NaI + 2 CO_2 + H_2O.$$
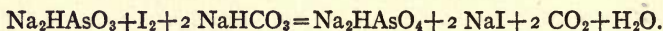
6. Since the addition of iodine in excess to the weakly basic bicarbonate solution is likely to lead to a slight degree of action, it is best in this titration not to overstep the end-point.

7. Iodine is a rather expensive chemical and it is well worth while to recover it from the united residues of a large class.

THE DETERMINATION OF ANTIMONY IN STIBNITE

The sample for analysis should be an antimony ore, practically free from arsenic and iron, and with hydrochloric acid it should leave only a siliceous residue.

Procedure. Weigh out two 0.20 g. portions of the finely ground mineral into dry 150-cc. beakers. Cover the beakers, add 5 cc. of 12-normal hydrochloric acid, and allow the acid to act in the cold for 10 minutes; then heat gently on the steam bath, for about 15 minutes, until the residue is white. Add 2 g. of powdered tartaric acid and gently warm the mixture for 10 minutes longer. Do not allow the liquid to evaporate sufficiently to expose any part of the bottom of the beaker. Dilute the solution cautiously with 5-cc. portions of water; if a red coloration appears, stop the dilution, warm until the solution is colorless, and again dilute. Continue the dilution

until a volume of 100 cc. is reached, and boil for a minute. Neutralize the clear, cold solution with sodium hydroxide (methyl orange), and then acidify it with dilute hydrochloric acid, a drop or two in excess.

Dissolve 10 g. of sodium bicarbonate in 400 cc. of water, place 200 cc. of this solution in each of two 700-cc. beakers, and transfer to these the cold solutions of the ore, avoiding loss by effervescence. Add 5 cc. of starch solution, and titrate each mixture with the standard iodine solution, to the appearance of the blue color. Do not overstep the end-point.

From the corrected data, calculate the percentage of antimony in the stibnite.

NOTES. — 1. Stibnite is essentially native antimony sulphide, Sb_2S_3, and upon treatment with hydrochloric acid hydrogen sulphide is liberated; but this is partially absorbed by the acid. The gas should be wholly expelled during the heating on the steam bath; if it is not completely driven out, antimony sulphide will begin to separate at some point in the dilution. In that case, however, if the dilution is at once stopped and the solution heated, the hot acid will redissolve the sulphide, and the hydrogen sulphide may then be expelled. The final boiling is to insure the absence of hydrogen sulphide, which itself reacts with iodine.

2. Antimony trichloride in the presence of strong hydrochloric acid is somewhat volatile, and for this reason the solution should not be boiled before dilution. If the solution is gently heated as described, no error need be feared from this source.

3. If, for any reason, a white precipitate of oxychloride separates during the dilution or neutralization, it is best to reject the solution and start anew. Antimony chloride is readily hydrolyzed upon dilution, with the precipitation of basic compounds such as SbOCl; but the addition of tartaric acid leads to the formation of stable antimonyl tartrates, which are soluble. In this way the antimony is kept in solution.

4. The reaction between the iodine and the antimonyl tartrate is not so simple, but for purposes of calculation it is accurately expressed by the equation, $Sb_2O_3 + 2\,I_2 + 2\,H_2O \rightleftarrows Sb_2O_5 + 4\,HI$. The purpose of the bicarbonate is here also to neutralize the hydriodic acid formed, and thereby drive the oxidation to completion.

5. The sodium hydroxide is added merely to neutralize most of the acid, and to make it easy to provide for the presence of a known amount of

sodium bicarbonate. The solution should be slightly, but distinctly, acid when the bicarbonate is added.

6. If the ore to be analyzed contains more than traces of iron, it is dissolved in hydrochloric acid, the antimony is precipitated with hydrogen sulphide, and the washed precipitate is redissolved in hydrochloric acid and determined as above. In case arsenic also is present, a somewhat more complicated separation of the antimony is necessary.

THE DETERMINATION OF LEAD IN AN ORE

Procedure. Weigh out two samples of the finely ground ore sufficient to contain about 0.20 g. of lead (0.28–0.29 g. of a 70% ore), and treat each as follows: Moisten the sample with water, add 15 cc. of 12-normal hydrochloric acid, and evaporate on the steam bath to about 5 cc. Add 3 cc. of strong nitric acid, evaporate nearly to dryness, then add 20 cc. of 6-normal hydrochloric acid and again heat to bring all the lead chloride into solution. Add 20 cc. of 6-normal sulphuric acid and evaporate to white fumes. Allow to cool, add 50 cc. of water, boil, and then add 15 cc. of alcohol; stir, allow to settle, and filter. Wash the lead sulphate and gangue six times with 10-cc. portions of 0.5-normal sulphuric acid (15 cc. of 6-normal acid in 165 cc. of water), transfer the residue to a small beaker by means of a jet of water, and heat it gently for a few minutes with 20 cc. of ammonium acetate solution;[1] filter the liquid through the original filter and wash the latter with small portions of the hot ammonium acetate solution. Dilute the extract to 150 cc., heat to boiling and add from a pipette 10 cc. of potassium dichromate solution.[2] Boil the mixture gently for 10 minutes, filter off the precipitate of lead chromate and wash the filter and precipitate about ten times with 10-cc. portions of dilute ammonium acetate solution (25 cc. of the extraction solution diluted to 250 cc.), until the excess of potassium chromate is completely removed.

[1] Made by neutralizing 30% acetic acid with 6-normal ammonia, and then adding a slight excess of ammonia.

[2] A solution containing 75 g. of $K_2Cr_2O_7$ per liter.

Now place a clean 500-cc. Erlenmeyer flask under the funnel, and with a jet of cold, acid, sodium chloride solution [1] stir up and dissolve the precipitate; continue washing with the same liquid until every trace of color is removed from the filter. In any case, use at least 50 cc. of the liquid. Finally dilute to 150 cc., add 1 g. of potassium iodide, mix, and titrate at once with a solution of sodium thiosulphate (which has been standardized in the same way against test lead, see Note 5) until the brown color becomes faint; then add 5 cc. of starch solution, and continue the titration cautiously until the solution becomes pale green ($CrCl_3$) with no tinge of blue. The end-point is very sharp, but without great care it may easily be passed. It is best to have a white surface under the flask.

Report the percentage of lead in the ore.

Notes. — 1. The ore is first heated with strong hydrochloric acid in order to expel most of the sulphur. Nitro-hydrochloric acid is then used to decompose any refractory sulphides. Upon evaporating the chloride solution to white fumes with sulphuric acid, the volatile acids in which lead sulphate is slightly soluble are completely expelled, and upon dilution with water, especially if alcohol is added, the lead is all left in the residue as lead sulphate.

2. Lead sulphate is readily dissolved by ammonium acetate solution, owing to the exceptional behavior of lead acetate with respect to ionization (see Part I), leaving the siliceous gangue, $BaSO_4$, etc., as a residue.

3. While lead is not precipitated from solutions containing a large excess of acetate ion by sulphates, the addition of a soluble chromate causes the precipitation of lead chromate. This behavior is due to the fact that such solutions contain Pb^{++}-ion at an extremely low concentration (owing to the presence of the lead mainly in the form of intermediate or complex ions, as $(Pb \cdot C_2H_3O_2)^+$, $[Pb(C_2H_3O_2)_3]^-$, etc.), and also to the fact that lead sulphate is very much more soluble than lead chromate; the lead-ion concentration is still great enough in such solutions to cause the solubility product of lead chromate to be exceeded upon the addition of potassium chromate in excess.

4. The solubility of lead chromate in the acid chloride solution is due on the one hand to the lowered concentration of the chromate ion, owing to

[1] Mix 10 cc. of 12-normal hydrochloric acid with 15 cc. of water, and add this mixture to 100 cc. of a saturated solution of sodium chloride.

the formation of non-ionized H_2CrO_4, $HCrO_4^-$, etc., and on the other hand to the great tendency of lead ion to form soluble complexes with chloride solutions. (Cf. the solubility of silver chloride in chloride solutions.)

5. The reaction of the acid solution with potassium iodide is most simply represented by the equation,

$$Cr_2O_7^{--} + 6 I^- + 14 H^+ = 2 Cr^{+++} + 7 H_2O + 3 I_2;$$
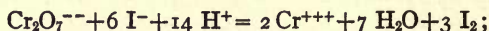
from this it may be seen that one atom of lead (as $PbCrO_4$) leads to the liberation of 3 atoms of iodine. But the results vary slightly with the conditions, and for that reason the thiosulphate solution must be standardized under identical conditions against a known amount of lead. In this case, 0.20 g. of test lead should be dissolved in 5 cc. of 6-normal nitric acid, the solution evaporated to white fumes with 20 cc. of 6-normal sulphuric acid, and the subsequent operations carried out as described in the procedure.

THE DETERMINATION OF COPPER IN AN ORE

Principle. This method is based upon the reaction which takes place upon the addition of potassium iodide to a slightly acid copper salt solution; cuprous iodide is precipitated as a cream-colored powder, and iodine is set free:

$$2 CuSO_4 + 4 KI = 2 K_2SO_4 + Cu_2I_2 + I_2.$$
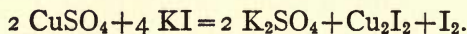
The iodine is promptly titrated with a standard thiosulphate solution.

Standardization of the Thiosulphate Solution. Weigh accurately two portions of pure bright copper wire or foil, of 0.15–0.16 g. each, and, in 250-cc. Erlenmeyer flasks, dissolve these in 5-cc. portions of 6-normal nitric acid. Dilute each solution to 15 cc. and boil to expel the red fumes; then dilute to 25 cc. and add ammonia (sp. gr., 0.90) in slight excess. Again boil until the ammonia odor is faint, add 80% acetic acid, 2–3 cc. in excess, and boil for a moment longer, agitating the flask in a holder to prevent bumping. Cool to room temperature, dilute to 40 cc., add a solution of 3 g. of potassium iodide in 10 cc. of water, and titrate at once with the approximately tenth-normal thiosulphate solution to a faint brown tinge; add 5 cc. of starch solu-

tion, and continue the titration until the last faint lilac tint is removed by a single drop. Do not overstep the end-point. From the data obtained, calculate the value of the solution per cubic centimeter in terms of copper.

Analytical Procedure. Weigh out into 300-cc. beakers samples of the ore sufficient to furnish about 0.15 g. of copper, and treat each as follows: Add 10 cc. of hydrochloric acid (sp. gr., 1.19) and 5 cc. of nitric acid (sp. gr., 1.42) and heat in the covered beaker on the hot plate until decomposition is complete, adding more of the acids if necessary, and enough water at the end to hold all soluble salts in solution. Then add 15 cc. of 6-normal sulphuric acid, and continue the heating until abundant white fumes begin to come off. Cool, add 50–60 cc. of water, boil for a moment, and allow to stand, hot, until any anhydrous ferric sulphate has dissolved. Finally, filter off from any lead sulphate, gangue, and sulphur, receiving the filtrate and washings in a 300-cc. beaker. Now add a solution of 5 g. of sodium thiosulphate in 25 cc. of water, boil to coagulate the precipitate, and filter, transferring the precipitate quantitatively to the filter by means of hot water. Dry the precipitate on the filter.

Place the precipitate, together with the filter, in a porcelain crucible, ignite gently until the filter is consumed, and allow to cool. Transfer the bulk of the precipitate to a 250-cc. Erlenmeyer flask, and set aside. To dissolve the last portions of the precipitate from the crucible, add 3 cc. of concentrated nitric acid and 2 cc. of water, and warm gently on the hot plate, finally pouring the acid solution into the flask containing the bulk of the precipitate, and washing out the crucible with a few small portions of 6-normal nitric acid. Heat the mixture in the flask until the decomposition is complete, dilute to 25 cc., boil, add ammonia in slight excess, and heat until the odor is faint. Add 80% acetic acid, 2–3 cc. in excess, and boil for a moment, vigorously agitating the flask to prevent bumping. Cool to room temperature, dilute to 40 cc., add 3 g. of potassium iodide dissolved in 10 cc. of water, and titrate at once with the thio-

sulphate solution, as previously described. Report the percentage of copper in the ore.

NOTES. — 1. Since iron and other elements likely to be present interfere with the process, the copper must be separated from these. Lead is first removed by means of sulphuric acid, after which the copper is precipitated from the hot, acid solution by means of sodium thiosulphate; this gives a flocculent precipitate of cuprous sulphide mixed with sulphur, which filters readily and can be washed with hot water without fear of oxidation. Arsenic and antimony, if present, are also precipitated, but under the treatment prescribed the usual quantities of these elements are without influence. They are mostly volatilized during the ignition. If antimony is present in appreciable quantity, it is perhaps better to filter the solution before the addition of the ammonia.

2. In order to obtain the best results it is necessary to standardize the thiosulphate solution against pure metallic copper. When this is done the method is very accurate; otherwise the results are not so good. For example, a thiosulphate solution which (titrated against a freshly standardized iodine solution) had a calculated copper value of 0.00608 g. per cubic centimeter, was found upon standardization against pure copper to have a value of 0.00611 g. per cubic centimeter.

3. Since nitrous fumes liberate iodine from potassium iodide, they must be completely expelled by boiling before the addition of the salt. The expulsion of the last traces of these fumes is insured by boiling the solution after it has been acidified with acetic acid.

4. The return of the blue tinge in the liquid after long standing is of no significance, but a quick return which is not prevented from recurring by the addition of a single drop of the thiosulphate solution is usually an evidence of faulty work.

5. In such a case, or if the end-point has accidentally been passed, the same sample may be prepared anew for titration: Add 10 cc. of concentrated nitric acid, and heat very cautiously, with great care not to allow the mixture to foam over. After most of the iodine has been expelled, manipulate the flask (in a holder) over a free flame and boil the solution down rapidly to a volume of 5–10 cc. Dilute to 25 cc. with water, boil, add ammonia in slight excess, and finish as described in the procedure.

6. In the electrolytic determination of copper in ores containing arsenic and other interfering substances, a satisfactory copper solution is most readily prepared by dissolving the ignited thiosulphate precipitate in a suitable quantity of strong nitric acid, with subsequent dilution to the required volume.

C. PRECIPITATION METHODS

General Discussion. The completion of neutralization reactions depends upon the very slight degree of ionization of one of the products, water. The completion of reactions of oxidation and reduction most often depends upon the relative potentials of oxidizing and reducing agents under specific experimental conditions. Certain other reversible reactions which serve as the basis of volumetric processes run to completion in consequence of the formation of very slightly soluble precipitates. In most cases an indicator is used, but in some the cessation of precipitation with the further addition of the standard solution indicates the completion of the reaction.

An example of the latter kind is found in Gay-Lussac's method for silver, which dates from 1832, and which is still widely used in determining the fineness of silver bullion. When silver chloride first separates it is finely divided, and a very minute quantity can easily be recognized; if the solution is shaken vigorously the precipitate coagulates and settles, leaving a supernatant liquid which is perfectly bright and clear. Hence, if silver nitrate is titrated with a solution of sodium chloride and the mixture well shaken in a stoppered bottle after each addition, the point at which the addition of a further quantity of the standard solution fails to produce a precipitate can readily be determined. Near the end-point it is customary to use a standard solution ten times as dilute as that used at the start.

In the case of this reaction, this method of determining the end-point admits of a very high degree of accuracy, and it is the method in use at the government mints. Since, however, it is rather tedious and demands considerable skill and experience, a slightly less accurate but much more convenient method is generally employed.

Silver thiocyanate is even less soluble than silver chloride, and it is therefore possible to titrate silver very accurately with a standard solution of potassium or ammonium thiocyanate. If a

solution of a ferric salt, acidified to suppress hydrolysis, is present as an indicator, the first drop of thiocyanate solution in excess will impart to the mixture a pink tint. This method (Volhard's) is also suitable for the determination of the halogens (except fluorine) and of certain other ions which give silver compounds insoluble in dilute nitric acid. A measured volume of standard silver nitrate solution is added in excess, and the excess is then determined by means of the standard thiocyanate solution.

THE PREPARATION AND STANDARDIZATION OF APPROXIMATELY ONE–TENTH NORMAL SOLUTIONS OF SILVER NITRATE AND POTASSIUM THIOCYANATE

Procedure. Dissolve 5.0 g. of potassium thiocyanate (or the equivalent quantity of the ammonium salt) in water and dilute the solution to 500 cc. Also dissolve 8.5 g. of silver nitrate in water and dilute the solution to 500 cc. Further, mix 10 cc. of 6-normal nitric acid with 40 cc. of water, heat the solution to boiling, and dissolve in the hot liquid 5 g. of pure ferric alum. Allow the solution to cool, and keep it for use as an indicator.

Now fill the burettes with the respective solutions, placing the silver nitrate solution in a glass-stoppered burette. (Observe the usual precautions to prevent dilution, and *place all solutions and precipitates containing silver in the receptacle for silver residues.*) Run out 20 cc. of the silver nitrate into a beaker, dilute to 150 cc., add 10 cc. of 6-normal nitric acid which has been recently boiled, and 5 cc. of the indicator solution. Run in the thiocyanate solution until, after vigorous stirring, a faint pink tinge can be detected in the solution. If the end-point is overstepped, titrate back with the silver nitrate solution. From the corrected volumes used, calculate the ratio of the thiocyanate to the silver nitrate solution. Repeat until the results do not differ by more than two parts in one thousand.

Finally, standardize the silver nitrate solution, as follows: Weigh out portions of pure sodium chloride, of 0.12–0.14 g. each, dissolve these in 75-cc. portions of water, heat to boiling,

and with stirring run into each from a burette 25.00 cc. of the silver nitrate solution. Add 10 cc. of freshly boiled 6-normal nitric acid, stir, and filter, washing the precipitate by decantation with several small portions of hot distilled water, and pouring these slowly over the filter; the united filtrate and washings should have a volume of about 150 cc. To this solution add 5 cc. of the indicator, and titrate the excess of silver with the thiocyanate solution, as already described. From the data obtained, calculate the normality factor of the silver nitrate solution; and from the mean of the duplicate values, which should agree within two parts in a thousand, calculate the normality factor of the thiocyanate solution.

NOTES. — 1. The reactions between the thiocyanate and the indicator are essentially as follows:

$$Fe^{+++} + 6\ CNS^- \rightleftarrows Fe(CNS)_3 + 3\ CNS^- \rightleftarrows [Fe(CNS)_6]^{---}.$$
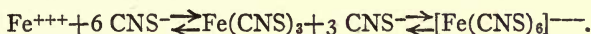
It will be recalled that in testing for ferric iron with potassium thiocyanate, it is necessary to add a large excess of the latter in order to detect the smallest possible quantity of iron. In the same way, when using ferric iron as an indicator for thiocyanate, it is necessary to provide a high concentration of the former in order to detect the slightest possible excess of the thiocyanate in the solution. The reactions which give rise to the colored substances are reversible, but in the presence of a large excess of one of the colorless constituents the dissociation of the colored substances is prevented by mass action.

2. Nitric acid is added to the solution to be titrated in order to prevent the hydrolysis of the ferric salt, which would impart a brownish red color to the mixture. It is boiled to free it from nitrous fumes, though this is of less importance here than in testing for iron in the presence of nitric acid; nitrous fumes color the thiocyanate pink.

3. Sodium chloride may easily be obtained pure by filtering a concentrated solution of the commercial salt, saturating it with hydrogen chloride gas, and filtering off the precipitate. The latter is washed with strong hydrochloric acid and dried at 150°, or higher.

4. Standard solutions of silver nitrate can of course be prepared by the solution of the calculated amount of pure metallic silver in nitric acid, and dilution to the required volume; or by means of the calculated weight of pure silver nitrate.

THE DETERMINATION OF CHLORINE IN A SOLUBLE CHLORIDE

The sample may be an artificial mixture of the chloride and carbonate of sodium.

Procedure. Weigh out into 300-cc. beakers, two portions, each sufficient to contain about 0.12 g. of sodium chloride, and treat each as follows: Dissolve the sample in 50 cc. of water, run in from a burette 30.00 cc. of the standard silver nitrate solution, and carefully acidify the mixture with dilute nitric acid. Heat to boiling, see that the liquid is distinctly acid, and filter. Receive the filtrate and washings in a 300-cc. Erlenmeyer flask. To the united filtrate and washings, which should have a volume of about 150 cc., add 10 cc. of 6-normal nitric acid and 5 cc. of the indicator solution, and titrate with the standard thiocyanate solution, as already described. Calculate the percentage of chlorine in the sample.

NOTES. — 1. Since silver chloride is several times as soluble as silver thiocyanate, the former must be filtered off before the titration of the excess of silver nitrate; otherwise the silver chloride would react with the thiocyanate solution and render the end-point uncertain. This behavior is best represented by the following system of equilibria:

$$AgCl \rightleftarrows AgCl \rightleftarrows \begin{cases} Cl^- + \\ Ag^+ \end{cases} (+CNS^- \rightleftarrows AgCNS \rightleftarrows AgCNS).$$
$$\quad (Solid) \quad (Diss'd) \qquad\qquad\qquad\qquad (Diss'd) \quad (Solid)$$
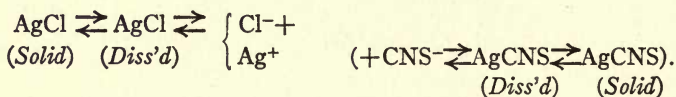
That is, if the silver chloride were left in the mixture during the titration, owing to the slow conversion of the soluble (colored) thiocyanate compounds into insoluble silver thiocyanate, there would be no permanent end-point.

2. Silver bromide and silver iodide are less soluble than silver thiocyanate, so that in the determination of bromine and iodine by this method it is not necessary to filter.

3. Soluble chlorates, etc., may be determined by this method by first reducing them to the corresponding halides (*e.g.* with sulphurous acid), and then determining the latter.

4. For other uses of precipitation methods, see Part IV, Problems, 90 91, 92, and 93.

PART IV

STOICHIOMETRY

Preliminary Discussion. The stoichiometrical problems met with in analytical work are, as a rule, neither hard to comprehend nor difficult to solve. The beginner will find that a moderate amount of time devoted to the intelligent study of these problems will enable him rapidly to make the calculations necessary for the interpretation of analytical data; the ability to do this is at least as important as the manipulative skill by which the data are obtained.

It cannot be too strongly emphasized that, in making such calculations, the beginner should from the outset strive to take the shortest and most direct route to the result. With a little practice, the student who is not unacquainted with the reactions of analytical chemistry should soon acquire the ability to recognize at once, upon the inspection of a problem, the factors which will lead most directly to its solution,[1] as well as the equivalent

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[1] Of course most analytical problems can be solved in stages, by means of a series of proportions, and it is perhaps only natural that most beginners should have a predilection for this method. In the examples given, however, the common factors have been eliminated, and the problems solved in a single operation. The beginning student will better appreciate the advantages of the shorter method upon comparing the solutions given of problems IV and V with the following roundabout method of arriving at the same results:

iv.   (*a*) $10 \, Fe : 2 \, KMnO_4 = 0.005 : w.$

$w = 316/558 \times 0.005 = 0.00283$ g. $KMnO_4$ per cc.

        (*b*) $2 \, KMnO_4 : 5 \, H_2C_2O_4 = 0.00283 : x.$

$x = 450/316 \times 0.00283 = 0.00403$ g. $H_2C_2O_4$ per cc.

        (*c*) $5 \, H_2C_2O_4 : 5 \, CaC_2O_4 = 0.00403 : y.$

$y = 640/450 \times 0.00403 = 0.00573$ g. CaC_2O_4 per cc.

        (*d*) $5 \, CaC_2O_4 : 5 \, CaO = 0.00573 : z.$

$z = 280.5/640.5 \times 0.00573 = 0.00251$ g. CaO per cc.   *Ans.*

relationships of the substances involved. *To do this, however, he should understand and bear in mind the relationships and differences which exist between chemical and physical units, — such as atoms, molecules, and equivalents on the one hand, and grams and cubic centimeters on the other.*

Detailed solutions of a few typical problems are given below. The student should study these carefully until they are fully understood.

i. A sample of a soluble chloride weighing 0.2007 g. yields on analysis 0.4920 g. of silver chloride; what percentage of chlorine does it contain?

From the proportion,

Wt. of chlorine in sample : Wt. of sample = % of chlorine : 100,

it is obvious that $\dfrac{\text{Wt. of chlorine in sample}}{\text{Wt. of sample}} \cdot 100 = \%$ of chlorine.

Also, since the chlorine contained in the sample is identical with that which is later contained in the silver chloride precipitate, we have the proportion,

$$Cl : AgCl = \text{Wt. of chlorine} : \text{Wt. of silver chloride,}$$

or, $\dfrac{Cl}{AgCl} \cdot$ Wt. of silver chloride = Wt. of chlorine.

Substituting this value in the preceding equation, we get,

$$\frac{\dfrac{Cl}{AgCl} \cdot \text{Wt. of silver chloride}}{\text{Wt. of sample}} \cdot 100 = \frac{\dfrac{35.46}{143.34} \cdot 0.4920}{0.2007} \cdot 100$$

$$= 60.50\% \text{ of Cl.}$$

v.   (*a*) $AgCl : HCl = 0.1527 : x.$
       $x = 36.46/143.34 \times 0.1527 = 0.0388$ g. HCl in 20.50 cc.
     (*b*) $20.50 : 1000 = 0.0388 : y.$
       $y = 1000/20.5 \times 0.0388 = 1.893$ g. HCl in one liter.
     (*c*) $36.46 : 1.893 = 1 : z.$
       $z = 1.893/36.46 = 0.0519 \ N.$ *Ans.*

A *chemical factor* expresses the quantity by weight of an element or compound which is *equivalent* to one part by weight of some other substance. For example, the ratio or factor

$$\frac{Ag}{AgCl} = \frac{107.88}{143.34} = 0.7526$$

tells us that one gram of silver chloride contains 0.7526 g. of silver, and if we wish to calculate what weight of silver there is in a specific weight of silver chloride, we simply multiply the latter by this factor; *e.g.* 10.15 g. of silver chloride contain 10.15 × 0.7526 = 7.64 g. of silver.

Again, if the weight of FeO which corresponds to a specific weight of Fe_2O_3 is desired, the factor is

$$\frac{2\ FeO}{Fe_2O_3} = \frac{143.68}{159.68} = 0.8998$$

And, similarly, if it is wished to find the weight of K_2O which corresponds to a specific weight of KCl, the factor is

$$\frac{K_2O}{2\ KCl} = \frac{94.20}{149.12} = 0.6317$$

In the calculation of these (physical-unit) factors, the equivalent relations of the two substances must be kept clearly in mind; thus it is plainly *incorrect* to express the ratio of potassium oxide to potassium chloride by the fraction $\frac{K_2O}{KCl}$, since each molecule of K_2O must yield upon treatment with HCl two molecules of KCl. Similarly, the factor for the conversion of $Mn_2P_2O_7$ into Mn_3O_4 is $\frac{2\ Mn_3O_4}{3\ Mn_2P_2O_7}$; for two molecules of Mn_3O_4, containing six atoms of manganese, will yield three molecules of $Mn_2P_2O_7$, also containing six atoms of manganese. Carelessness in this respect is one of the most frequent sources of error.

ii. How many cubic centimeters of a solution containing 25 grams of $BaCl_2 . 2 H_2O$ per liter will be required to precipitate the sulphur from 0.1073 gram of pure stibnite, Sb_2S_3, as $BaSO_4$?

M

Each molecule of Sb_2S_3 will yield upon treatment three molecules of H_2SO_4, and these will require three molecules of barium chloride for precipitation. We therefore arrive at the proportion, $3 (BaCl_2 \cdot 2 H_2O) : Sb_2S_3 = x : 0.1073$, where x represents the weight of the crystalline salt required. That is,

$$x = \frac{3 (BaCl_2 \cdot 2 H_2O)}{Sb_2S_3}$$

in which the factor $\dfrac{3 (BaCl_2 \cdot 2 H_2O)}{Sb_2S_3} = 2.177$ indicates the quantity by weight of $BaCl_2 \cdot 2 H_2O$ which is required to precipitate the sulphur from one gram of Sb_2S_3; this factor therefore does not differ essentially from the chemical factors previously discussed.

Finally, since each cubic centimeter of the solution contains 0.025 g. of $BaCl_2 \cdot 2 H_2O$, we have,

$$\frac{\dfrac{3(BaCl_2 \cdot 2 H_2O)}{Sb_2S_3} \cdot 0.1073}{0.025} = \frac{\dfrac{732.9}{336.6} \cdot 0.1073}{0.025} = 9.34 \text{ cc.}$$

iii. What volume of aqueous ammonia of sp. gr. 0.960, containing 9.91% of NH_3, will be required to precipitate, as $Fe(OH)_3$, the iron contained in 1.475 g. of $Fe(NH_4SO_4)_2 \cdot 6H_2O$?

Since the iron is to be precipitated, after oxidation, as $Fe(OH)_3$, it is plain that each atom of iron will require three molecules of NH_4OH, which in turn are furnished by three molecules of NH_3. Therefore, $\dfrac{3 NH_3}{Fe(NH_4SO_4)_2 \cdot 6H_2O} \cdot 1.457 = $ wt. of NH_3 required; and, since each cubic centimeter of the aqueous ammonia weighs 0.960 g., and contains 9.91% of NH_3, the solution contains 0.960×0.0991 g. of NH_3 per cubic centimeter. That is,

$$\frac{\dfrac{3 NH_3}{Fe(NH_4SO_4)_2 \cdot 6 H_2O} \cdot 1.457}{0.960 \times 0.0991} = \frac{\dfrac{51.10}{392.16} \cdot 1.475}{0.960 \times 0.0991} = 2.02 \text{ cc.}$$

iv. A solution of potassium permanganate is equivalent to 0.00500 g. of ferrous iron per cubic centimeter; what is its value in terms of calcium oxide?

The reactions involved in the volumetric determinations of iron and calcium are:

$$10\ FeSO_4 + 2\ KMnO_4 + 9\ H_2SO_4 = 2\ KHSO_4 + 2\ MnSO_4$$
$$+ 5\ Fe_2(SO_4)_3 + 8\ H_2O,$$

and

$$5\ CaC_2O_4 + 2\ KMnO_4 + 9\ H_2SO_4 = 5\ CaSO_4 + 2\ KHSO_4$$
$$+ 2\ MnSO_4 + 10\ CO_2 + 8\ H_2O;$$
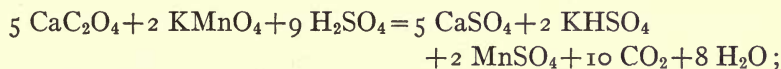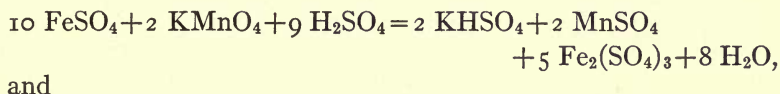
and from these equations it is clear that, in this case, $2\ Fe^{++} \backsimeq CaO$. That is,

$$\frac{CaO}{2\ Fe} \cdot 0.00500 = \frac{56.1}{111.6} \cdot 0.00500 = 0.00251\ g.\ CaO.$$

v. If 20.50 cc. of hydrochloric acid yield 0.1527 g. of silver chloride, what is the normality factor of the solution?

Although silver chloride is insoluble, the normality factor of the acid may nevertheless be calculated directly from the weight of the precipitate obtained. One liter of normal hydrochloric acid, containing one mol of HCl, would yield 143.34 g. (*i.e.* one mol) of silver chloride, whence 20.50 cc. would yield 0.14334 ×20.50 g. We obtain, therefore, the equation,

$$\frac{0.1527}{0.14334 \times 20.50} = 0.0519\ N.$$

vi. A sample of stibnite weighing 0.1793 g. is heated with strong HCl, and the H_2S evolved absorbed by means of sodium hydroxide solution; the resulting mixture (containing the sulphur as Na_2S) being introduced under the surface of a solution made by adding 25 cc. of 6-normal HCl and 50.00 cc. of 0.1160-normal iodine to 500 cc. of water. The excess of iodine is titrated with 0.0957-

normal sodium thiosulphate solution, of which 28.57 *cc. are required.   Calculate the percentage of (evolved) sulphur in the stibnite.*

($H_2S + I_2 = 2\ HI + S$.)
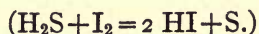
cc.   N. F.

50.00 × 0.1160 = 5.800 cc. of normal iodine.

28.57 × 0.0957 = 2.734 cc. of normal thiosulphate.

I.e. the H_2S required   3.066 cc. of normal iodine.

Since normal iodine has a sulphur value of $\dfrac{0.03207}{2} = 0.016045$ g. per cubic centimeter, we have,

$$\frac{0.016035 \times 3.066}{0.1793} \times 100 = 27.42\% \text{ of sulphur.}$$

The *normality factor* of a solution expresses the value of the solution per cubic centimeter in terms of a normal solution. For example, if a solution is known to be one half normal (*i.e.* N. F. = 0.500), it is obvious that 1 cc. of it is equivalent to 1.000 × 0.500 = 0.500 cc. of a normal solution; or that 27.31 cc. of it are equivalent to 27.31 × 0.500 = 13.655 cc. of a normal solution.   Knowing the normality factors of a series of solutions, therefore, we can readily reduce the different volumes of the solutions used in a determination to a common standard; and in this way the calculations are rendered almost as simple as if the time and labor had been expended to make the solutions all of exactly the same strength, say one-tenth normal.

vii. Indirect methods of analysis depend upon the fact that when two or more substances are made to undergo the same chemical treatment they either experience a relatively different change of weight, or unit weights of each require unequal volumes of a standard solution.

For example, suppose we wish to determine the weight of NaCl and of KCl in a mixture of the two salts.   The mixture, weighing a grams, may be converted into silver chloride, of which there is formed, say, p *grams.*

Let x represent the weight of the sodium chloride, and y that of the potassium chloride, and we have,

$$x+y=a,$$

and

$$\frac{AgCl}{NaCl}x+\frac{AgCl}{KCl}y=p.$$

If we designate by m the factor $\dfrac{AgCl}{NaCl}$ and by n the factor $\dfrac{AgCl}{KCl}$, we obtain,

$$x+y=a,$$

and

$$mx+ny=p,$$

from which we find that

$$x=\frac{p-na}{m-n},$$

or

$$x=\frac{1}{m-n}\cdot p-\frac{n}{m-n}\cdot a.$$

Indirect analyses may in general be calculated by means of this or a similar general equation.

In the above example,

$$m=\frac{AgCl}{NaCl}=\frac{143.34}{58.46}=2.4520,\quad n=\frac{AgCl}{KCl}=\frac{143.34}{74.56}=1.9223,$$

and

$$m-n=0.5297.$$

If these values are substituted in the general equation, we obtain,

$$x=1.888\,p-3.628\,a.$$

Consequently, in order to determine the weight of sodium chloride in the mixed sample it is only necessary to determine the values of a and p, multiply them by 3.628 and 1.888, respectively, and subtract the first product from the second.

The same analysis might be performed by weighing the mixed chlorides in a platinum crucible, then changing them to sulphates (by evaporation with H_2SO_4), and again weighing. In this case also,

$$x=\frac{1}{m-n}\cdot p-\frac{n}{m-n}\cdot a$$
$$=21.547\,p-25.181\,a.$$

In the first case, the coefficients are relatively small, and consequently good results might be expected, since the experimental errors made in the determination of a and p are multiplied by only 3.63 and 1.89, respectively. In the latter case, however, the coefficients are very large, and the unavoidable analytical errors would have to be multiplied enormously in the calculation; the method is therefore worthless.

Although some indirect methods may appear simple and attractive on paper, they frequently lead to impossible values in practice; so that extreme caution should be exercised regarding the use of an indirect method. *In general, if accurate and reliable results are desired, indirect methods of analysis should be avoided.*

PROBLEMS

GRAVIMETRIC ANALYSIS

1. Calculate the chemical factors for the following: KCl from K_2PtCl_6; K_2O from K_2PtCl_6; P from $Mg_2P_2O_7$; Fe_3O_4 from Fe_2O_3; MnO_2 from Mn_3O_4.

2. What weight of Mn_3O_4 corresponds to 0.5785 g. of $Mn_2P_2O_7$? To 0.4327 g. of $MnSO_4$?

3. A sample of an impure ammonium salt weighing 0.4988 g. is converted into $(NH_4)_2PtCl_6$, and this upon ignition yields 0.3258 g. of platinum. Calculate directly from the weight of platinum the percentage of NH_3 in the sample.

4. A sample of phosphorus pentoxide weighing 0.2018 g. yields 0.3132 g. of $Mg_2P_2O_7$. Calculate the percentage of P_2O_5 in the sample.

5. What weight of a silver nitrate solution known to contain 2.31% of Ag will be required to precipitate the chlorine from 25.0 cc. of a solution containing 25.0 g. of $BaCl_2 . 2 H_2O$ in one liter?

6. If 25.0 cc. of sodium chloride solution yield 0.1434 g. of silver chloride, what is the strength of the solution in grams of the salt per liter? In mols per liter?

7. How many cubic centimeters of a solution containing 25.0 g. of $BaCl_2 . 2 H_2O$ per liter will be required to precipitate, as $BaSO_4$, the sulphuric acid formed upon oxidizing 0.2543 g. of FeS_2 with fuming nitric acid?

8. How many cubic centimeters of hydrochloric acid of sp. gr. 1.050, containing 10.17% of HCl, will it take to precipitate the silver from a solution containing 0.8430 of silver sulphate?

9. How many cubic centimeters of hydrochloric acid of sp. gr. 1.040, containing 8.16% of HCl, will be required to dissolve one gram of calcium carbonate?

10. What weight of $Mn_2P_2O_7$ is it possible to prepare from 50.0 cc. of a permanganate solution which contains 4.500 g. of $KMnO_4$ per liter?

11. How many cubic centimeters of a solution of sp. gr. 1.116, containing 10.06% of $NaOH$, will it take to neutralize a solution containing 5.00 g. of $NaHSO_4$? 5.00 g. of $KHSO_4$?

12. A sample of impure potassium sulphide weighing 0.4320 g. is treated with hydrochloric acid, and by means of ammoniacal hydrogen peroxide solution the hydrogen sulphide evolved is converted into ammonium sulphate. This yields 0.8034 g. of $BaSO_4$. Calculate the percentage of K_2S in the sample.

13. A sample of stibnite weighing 1.078 g., upon being analyzed by the method indicated in Problem 12, yields 0.6750 g. of $BaSO_4$. Assuming the sulphur to be present wholly as Sb_2S_3, calculate the percentage of the latter in the mineral.

14. How many cubic centimeters of aqueous ammonia of sp. gr. 0.96, containing 9.91% of NH_3, will be required to precipitate the aluminum in 0.8674 g. of $KAl(SO_4)_2$. 12 H_2O? How many cubic centimeters of 6-normal ammonia?

15. What volume of the ammonia water first referred to in Problem 14 will it take to neutralize 10.0 cc. of hydrochloric acid of sp. gr. 1.12, containing 23.81% of HCl? To neutralize 10.0 cc. of 6-normal hydrochloric acid?

16. If 15.0 cc. of a solution of barium chloride yield, upon evaporation with hydrochloric acid and gentle ignition, 1.563 g. of the anhydrous salt, what is the strength of the solution in mols per liter? In equivalents per liter?

17. A solution contains 2.25% by weight of $BaCl_2$. What volume of a solution containing 5.000 g. of Ag_2SO_4 per liter will be required to precipitate the chlorine in 5.000 g. of the barium chloride solution? What will be the weight of the precipitate formed?

18. A sample of pyrite weighing 0.2500 g. yields upon analysis 0.8020 g. of $BaSO_4$. Upon the assumption that the sulphur is wholly present as FeS_2, calculate the percentage of the latter in the sample.

19. What volume of bromine water containing 30 g. of bromine per liter will be required to oxidize the iron in 1.75 g. of $FeSO_4$. 7 H_2O?

20. What volume of aqueous ammonia (sp. gr., 0.96, containing 9.91% of NH_3) will be required to precipitate the iron, after oxidation with hydrogen peroxide, from a solution containing 0.750 g. of $Fe(NH_4SO_4)_2$. 6 H_2O

and 12.0 cc. of hydrochloric acid (sp. gr., 1.12, containing 23.8% of HCl)?

21. A mixed sample of CaO, Ca(OH)$_2$, and CaCO$_3$ weighing 0.5896 g. is evaporated with excess sulphuric acid, and gently ignited; the residue weighs 0.8651 g. What volume of 6-normal hydrochloric acid will be required to convert 5.00 g. of the sample into calcium chloride?

22. The ignited precipitate of ferric and aluminum oxides from 1.497 g. of a mineral weighs 0.4196 g.; after ignition in a current of hydrogen the product weighs 0.3311 g., the ferric oxide being reduced to metallic iron. Calculate the percentage of Fe$_2$O$_3$ and of Al$_2$O$_3$ in the mineral.

23. A sample of pyrolusite weighing 0.5124 g. is heated in the presence of dilute sulphuric acid with an excess of oxalic acid, and the gas evolved is absorbed in a weighed bulb containing potassium hydroxide. The gain in weight of the bulb is found to be 0.4789 g. Calculate the percentage of MnO$_2$ in the pyrolusite.

24. What volume of 0.5-normal ammonium oxalate solution will be required to precipitate, as CaC$_2$O$_4$. H$_2$O, the calcium from one gram of apatite, [Ca$_3$(PO$_4$)$_2$]$_3$. CaF$_2$?

25. What volume of a solution containing 66 g. of (NH$_4$)$_2$HPO$_4$ per liter will be required to precipitate, as ZnNH$_4$PO$_4$, the zinc from 0.9786 g. of a brass which contains 30.15% of zinc? What is the normality of this solution as a precipitant for zinc?

26. How many grams per liter of K$_2$Cr$_2$O$_7$ must a solution contain in order that, by reduction of the chromium (with HCl and SO$_2$), precipitation with ammonia, and ignition of the precipitate in a current of hydrogen, a 50.0 cc. portion shall yield 0.3752 g. of Cr$_2$O$_3$?

27. What volume of a solution containing 25.0 g. of KH$_3$(C$_2$O$_4$)$_2$. 2 H$_2$O per liter will be required to precipitate the calcium from 0.976 g. of a limestone which yields, besides a small quantity of an insoluble residue, 2.14% of Fe$_2$O$_3$, 9.56% of MgO, and 45.36% of CO$_2$, assuming iron, magnesium, and calcium to be present wholly as carbonates (the iron of course as ferrous carbonate)?

28. What volume of 6-normal sulphuric acid will be required to replace the nitric acid in the salts obtained upon evaporating to dryness with nitric acid 4.984 g. of brass, if the brass contains 65.98% of Cu, 31.42% of Zn, 1.84% of Sn, and 0.76% of Pb?

29. A sample of silicate mineral weighing 1.0245 g. yields 0.2602 g. of potassium and sodium chlorides; and the mixed chlorides yield 0.4304 g. of K$_2$PtCl$_6$. Calculate the percentage of Na$_2$O in the sample.

30. A solution of chloroplatinic acid contains 0.050 g. of Pt per cubic centimeter. What is the minimum volume with which 0.2602 g. of mixed sodium and potassium chlorides must be evaporated in order to insure the

complete conversion of the alkali metals into chloroplatinates, no matter in what proportions the two chlorides may exist in the mixture?

31. A sample of phosphate rock contains 0.87% of moisture and 91.92% of calcium phosphate. Calculate the percentage of $Ca_3(PO_4)_2$ which is present on the dry basis.

32. If 2.497 g. of a fertilizer containing 4.45% of moisture yields 0.3150 g. of $Mg_2P_2O_7$, what is the percentage of P_2O_5 on the dry basis?

33. Upon treatment with sulphuric acid, 1.430 g. of a salt yields 0.5952 g. of Na_2SO_4 and 101.5 cc. of CO_2, measured moist at 17° C. and 757 mm. Calculate the percentages of Na_2O and CO_2 in the salt. (Tension of aqueous vapor at 17° = 14.45 mm.)

34. What weight of water is present in one liter of air which is 50% saturated with moisture at 17° and 748 mm.? (See problem 33.)

35. If in the analysis of a substance an error of 0.1% is unavoidable, how accurately is it necessary to weigh a sample of 200 mg.? A sample of five grams? (See p. 4.)

36. 1.3250 g. of pure Na_2CO_3 is dissolved in water and the solution made up accurately to 250.0 cc. A portion is carefully transferred without loss to a platinum dish by means of a pipette supposed to deliver 50.00 cc. of liquid. After evaporation with hydrochloric acid, and ignition, the sodium chloride residue is found to weigh 0.2927 g. What volume of this solution does the pipette actually deliver?

37. 0.7500 g. of a substance containing chlorine and bromine yields 0.5000 g. of Ag(Cl, Br). This mixture is heated in a current of chlorine, which converts the bromide of silver into the chloride, and the loss in weight due to this change is found to be 0.0683 g. Calculate the percentages of chlorine and bromine in the sample.

38. From the following data, calculate the percentage of each salt present in a mixture of sodium chloride, bromide, and iodide: Weight of sample, 0.1500 g.; weight of precipitate obtained by distilling the solution with nitrous acid and converting the iodine into silver iodide, 0.1056 g.; weight of silver chloride and bromide from the solution after removal of the iodine, 0.1784 g.; weight of this precipitate after conversion of the whole into silver chloride, 0.1623 g.

39. A sample of baking powder, which is known to contain only $NaHCO_3$ and $KHC_4H_4O_6$, in equivalent proportions, and starch, yields upon treatment with water 12.0% by weight of CO_2. Calculate the percentage of each salt in the sample.

40. A salt containing barium, chlorine, and water of hydration gave upon analysis the following data: Weight of sample, 1.0000 g.; weight after heating (water driven off), 0.8522 g.; weight of silver chloride ob-

tained, 1.1735 g.; weight of barium sulphate obtained, 0.9594 g. Calculate: (*a*) the percentage of each constituent; (*b*) the formula of the compound.

41. If two 1.0000-g. samples of a substance containing 10.00% of MgO are weighed out, and the precipitate of $MgNH_4PO_4 . 6 H_2O$ is in one case contaminated with 0.0250 g. of $Mg_3(PO_4)_2$, and in the other case with 0.0250 g. of $Mg[(NH_4)_2PO_4]_2$, what percentages of MgO will be found if the calculations are based upon the assumption that the ignited precipitate in each case consists entirely of $Mg_2P_2O_7$?

42. The carbonates of calcium, strontium and barium obtained from a 10-liter sample of mineral water are converted into the anhydrous nitrates, and the calcium nitrate is extracted with absolute alcohol-ether mixture. The residue is dissolved in water, the barium separated from the strontium, as $BaCrO_4$, and the strontium precipitated from the filtrate with sulphuric acid and alcohol. There are finally obtained 0.8507 g. of CaO, 0.1324 g. of $SrSO_4$, and 0.1072 g. of $BaCrO_4$; calculate the content of the water in milligrams per liter (*i.e.* parts per million) of Ca, of Sr, and of Ba.

43. How many cubic centimeters of sulphuric acid of sp. gr. 1.840, containing 95.6% of H_2SO_4, must be added to 1 liter of sulphuric acid of sp. gr. 1.560, containing 65.1% of H_2SO_4, to obtain a solution containing 75.0% of H_2SO_4?

44. A fuming sulphuric acid contains 25.5% of non-hydrated SO_3. How many grams of 98.2% H_2SO_4 must be added to 100 g. of the fuming acid to give a product containing 100% of H_2SO_4?

45. A limestone contains 90.0% of $CaCO_3$, 3.50% of $MgCO_3$, 3.00% of $CaSO_4 \cdot 2 H_2O$, 1.25% of $FeCO_3$, and 2.25% of anhydrous siliceous material. What numerical difference would you expect to find between the loss on ignition and the true percentage of CO_2?

46. An ore contains 28.15% of nickel, and 0.5000 g. samples are taken for analysis. In one sample the element is determined by electrolysis, as metallic nickel, while in a second sample it is determined by means of dimethylglyoxime, as $Ni(C_4H_7N_2O_2)_2$. If the algebraic sum of the errors involved in each determination were equivalent to a negative error of 1.7 mg. of the substance finally weighed, how much greater would the percentage error be in the first determination than in the second?

47. An electric current is passed simultaneously through a series of three electrolytic cells which contain water acidified with sulphuric acid, an ammoniacal solution of nickel sulphate, and molten silver chloride. What is deposited upon the cathode in each of the other cells, and how many grams, in the time in which one liter of hydrogen, measured moist at 17° and 746 mm., is liberated from the water? (Tension of aqueous vapor at 17° = 14.45 mm.)

48. From the following data, calculate the percentages of nickel and cobalt in the steel: Weight of sample, 1.124 g.; weight of nickel and cobalt obtained upon electrolysis, 0.1246 g.; weight of nickel dimethyl-glyoximine, $Ni(C_4H_7N_2O_2)_2$, obtained from the electrolytic deposit, 0.4382 g.

49. A mass of platinum weighs 12.145 g. in air, 11.580 g. in water, and 11.115 g. in sulphuric acid. What is the specific gravity of the platinum? Of the sulphuric acid?

50. A quantity of pure metallic silver weighing 1.0788 g. is dissolved in nitric acid and the solution made up to the mark in a measuring flask graduated to contain 100.0 cc. Three portions are carefully transferred without loss to three separate beakers by means of a pipette known to deliver 25.00 cc. If the solution remaining in the flask, together with the liquid finally washed from the pipette, yields on analysis 0.3560 g. of AgCl, what volume of liquid does the flask actually contain?

VOLUMETRIC ANALYSIS

51. If 25.00 cc. of hydrochloric acid yield 0.1435 g. of AgCl, what is the normality of the solution?

52. If a 25.00 cc. portion of acid requires 21.50 cc. of 0.526 N alkali for neutralization, what is the normality of the acid? Supposing the acid to be HCl, what weight of silver chloride will 10.00 cc. of it yield with silver nitrate?

53. If a 2.453 g. sample of pure anhydrous sodium carbonate requires 45.72 cc. of an acid for neutralization, and if 41.90 cc. of the acid requires 44.35 cc. of an alkali, what is the normality factor of each solution?

54. A sample of pure calcite, $CaCO_3$, weighing 2.150 g. is dissolved in 50.00 cc. of an acid, and the excess of acid is neutralized with 29.12 cc. of an alkali of which 28.40 cc. require 7.10 cc. of the acid for neutralization. To what volume must one liter of the acid be diluted in order to make it exactly normal?

55. How many cubic centimeters of 0.526 N acid will it take to neutralize the ammonia set free upon distilling 1.0378 g. of $MgNH_4PO_4 . 6 H_2O$ with an excess of caustic alkali?

56. If 15.25 cc. of alkali will neutralize 20.00 cc. of a solution containing 6.000 g. of $KH_3(C_2O_4)_2 . 2 H_2O$ in 250.0 cc., what is the normality factor of the alkali?

57. In the analysis of a feeding stuff, a Kjeldahl determination is carried out with a sample weighing 1.500 g. The ammonia is received in 25.00 cc. of 0.500 N acid, and the excess of acid is found to require 12.50 cc. of a standard alkali, of which 21.20 cc. will neutralize 18.00 cc. of the acid. Calculate the percentage of nitrogen in the sample.

58. What weight of crude cream of tartar must be taken for titration in order that twice the number of cubic centimeters of 0.2000 N alkali required may numerically equal the percentage content of $KHC_4H_4O_6$?

59. A sample of soda ash weighing 25.05 g. is dissolved and made up to 250.0 cc., and one fifth of this solution is taken for titration. What must be the normality of the standard acid (assuming the alkalinity to be due only to Na_2CO_3) in order that the burette reading multiplied by two may indicate the percentage of Na_2CO_3 in the sample?

60. A sample of caustic soda weighing 4.000 g. is dissolved in water and made up to one liter. A 100.0 cc. portion of this solution requires for neutralization 47.50 cc. of 0.2000 N acid. A second 100.0 cc. portion, after treatment with barium chloride in slight excess, is diluted to 200.0 cc. and allowed to settle, and 50.0 cc. of the clear solution require 11.50 cc. of the acid. Calculate the percentages of NaOH and Na_2CO_3 in the sample. (Neglect the volume occupied by the solid precipitate.)

61. A sample of Solvay soda weighing 3.750 g. is dissolved in water and made up to one liter. A 100.0 cc. portion of this solution, titrated in the cold with 0.1000 N acid, with the use of phenolphthalein, is found to require 29.95 cc. of the acid; the burette is then refilled and the titration completed at the boiling temperature of the solution, 35.15 cc. more of the acid being required. Calculate the percentages of Na_2CO_3 and $NaHCO_3$ in the sample. (Under suitable experimental conditions, phenolphthalein becomes colorless in the cold as soon as the carbonate has been wholly converted into bicarbonate.)

62. A sample of sirupy phosphoric acid weighing 5.767 g. is dissolved in water and made up to one liter. A 100.0 cc. portion of the solution is treated with sodium acetate and silver nitrate in excess, whereby the phosphate is quantitatively precipitated as Ag_3PO_4. Phenolphthalein is added to the filtrate and washings, and the solution titrated with 0.500 N alkali, of which 27.25 cc. are required. Calculate the percentage of H_3PO_4 in the original sample.

63. A sample of Chili saltpeter weighing 1.025 g. is treated in sodium hydroxide solution with pulverized Devarda's alloy (50% Cu, 45% Al, 5% Zn), which reduces the nitrogen to ammonia; the ammonia is distilled into 25.00 cc. of 0.463 N acid, and the excess of acid requires 5.01 cc. of 0.212 N alkali for neutralization. Assuming that nitrogen was wholly present as $NaNO_3$, calculate the percentage of the latter in the sample.

64. A sample of strontium nitrate weighing 10.53 g. is dissolved in water and made up to one liter. One tenth of this solution is distilled, in the presence of alkali, with an excess of titanous chloride, which reduces the nitrate to ammonia $(KNO_3 + 8\ Ti(OH)_3 + 6\ H_2O = KOH + 8\ Ti(OH)_4 + NH_3)$. The ammonia is received in 25.00 cc. of 0.500 N acid, and the excess of acid

requires 10.16 cc. of 0.250 N alkali. Assuming that the nitrogen was wholly present as $Sr(NO_3)_2$, calculate the percentage of the latter in the sample.

65. How many grams of $KH_3(C_2O_4)_2 \cdot 2 H_2O$ will it take to prepare one liter of a 0.500 N solution, to be used as a standard acid? How many to prepare one liter of a 0.1000 N solution, to be used as a reducing agent in connection with potassium permanganate?

66. How many grams of $K_2Cr_2O_7$ per liter will be required to prepare a solution of such strength that each cubic centimeter shall indicate 2.00% of iron, when a sample weighing 0.2792 g. is used for analysis? What is the normality factor of this solution?

67. From the following data, calculate the percentage of iron in the ore: Weight of sample, 0.2186 g.; the reduced iron solution requires for oxidation 25.14 cc. of 0.0996 N permanganate solution.

68. What is the maximum weight of an ore containing 70.00% of iron which can be taken for analysis without having to refill a 30-cc. burette, if the permanganate solution is 0.1025 N?

69. A calcium oxalate precipitate, obtained from 0.8432 g. of a rock, is decomposed with dilute sulphuric acid and made up to 250.0 cc.; of this a 50.0 cc. portion is titrated with 0.1012 N permanganate solution. If 27.35 cc. of the latter are required, what percentage of CaO does the rock contain?

70. 11.56 cc. of nitric acid of sp. gr. 1.19 are diluted to 250.0 cc.; 20.00 cc. of this solution are found to require 12.92 cc. of 0.410 N alkali. Calculate the percentage of HNO_3 in the acid of sp. gr. 1.19.

71. The Sb_2S_3 precipitate obtained from the solution of an ore is dissolved in sodium sulphide solution, and this is evaporated and fumed with an excess of sulphuric acid. The residue is then dissolved in dilute hydrochloric acid, and the antimony oxidized from the trivalent to the pentavalent condition by means of a standard solution of permanganate. The sample of ore weighs 0.2749 g. and 24.17 cc. of 0.1025 N permanganate solution are used in the titration; what is the percentage of antimony?

72. What is the normality factor of an acid, of which 25.37 cc. are equivalent to 1.263 g. of KNO_3 when the nitrogen of the latter is reduced in alkaline solution to ammonia and this is distilled off and received in the acid solution?

73. From the following data, calculate the percentage of MnO_2 in the ore: Weight of sample, 0.2000 g.; after heating this in the presence of sulphuric acid with 50.00 cc. of 0.1000 N oxalic acid, the excess of oxalic acid requires 8.50 cc. of 0.1000 N permanganate solution.

74. From the following data, calculate the percentage of MnO_2 in the ore: Weight of sample, 0.2400 g.; this is boiled with hydrochloric acid and the distillate received in an excess of potassium iodide solution,

the liberated iodine requiring 25.51 cc. of 0.2000 N sodium thiosulphate solution.

75. A sample of mineral substance weighing 1.000 g. is taken for analysis. In the determination of the iron, the ferric solution is completely reduced by means of sulphurous acid, and the excess of the latter removed by the passage of carbon dioxide through the boiling solution; the iron then requires 28.17 cc. of 0.1000 N permanganate solution. Calculate the percentage of iron in the substance.

76. What weight of pyrolusite containing 86.50% of MnO_2 will oxidize the same amount of oxalic acid as 50.0 cc. of a permanganate solution, if 10.00 cc. of the latter will liberate 0.1905 g. of iodine from an acidified solution of potassium iodide?

77. What weight of $Fe(NH_4SO_4)_2 . 6 H_2O$ will reduce 50.0 cc. of a permanganate solution, of which 10.00 cc. will liberate from an acidified solution of potassium iodide a quantity of iodine sufficient to react with 15.25 cc. of 0.1025 N thiosulphate solution?

78. A standard solution of permanganate will oxidize 0.00730 g. of ferrous iron per cubic centimeter; what is the value of the same solution in terms of (a) $H_2C_2O_4 . 2 H_2O$; (b) KNO_2; (c) H_2O_2; (d) $K_4Fe(CN)_6 . 3 H_2O$; (e) Mn?

79. The calcium oxalate precipitate obtained from 0.2500 g. of calcite is dissolved in an excess of sulphuric acid, and the hot solution titrated with a solution of permanganate of which each cubic centimeter represents 0.00735 g. of $Na_2C_2O_4$. If 45.57 cc. of the permanganate solution are required, what percentage of calcium does the mineral contain?

80. If 0.1340 g. of sodium oxalate require 19.23 cc. of a permanganate solution, how many milligrams of ferrous iron will each cubic centimeter of the permanganate solution indicate?

81. From the following data, calculate the percentage of manganese in the ore: Weight of sample, 0.5027 g.; volume of permanganate solution required to oxidize the manganese, 36.60 cc.; value of the permanganate solution for use with oxalic acid, 0.0997 N.

82. 2.400 liters of dry air (at 0°, 760 mm.) and 50.00 cc. of 0.0100 N barium hydroxide solution are shaken together, and the excess of alkali is found to require 35.06 cc. of 0.0100 N acid. What volume of carbon dioxide is contained in 10,000 volumes of the dry air?

83. If a permanganate solution is equivalent to 5.84 mg. of iron per cubic centimeter, what is the value of the solution in terms of $K_4Fe(CN)_6 . 3 H_2O$? In terms of N_2O_3?

84. What weight of iodine per cubic centimeter will be liberated by a permanganate solution from an excess of hydriodic acid, if the permanganate solution has an iron value of 4.98 mg. per cubic centimeter?

85. A sample of iron wire weighing 0.1408 g., and containing 99.8% of iron, is converted into ferrous chloride and titrated according to the Zimmermann-Reinhardt method; it requires 25.15 cc. of a permanganate solution. What weight of ore must be taken for analysis by the same method, in order that each cubic centimeter of the permanganate solution may indicate 2.50% of iron?

86. 25.00 cc. of a certain acid are found to require 23.67 cc. of an alkali. If 28.15 cc. of the acid are used to dissolve 0.5260 g. of pure calcium carbonate, and 6.61 cc. of the alkali are required to neutralize the resulting solution, what is the normality factor of the acid? What is that of the alkali?

87. The calcium oxalate precipitate from 0.5005 g. of a mineral requires, after decomposition with sulphuric acid, 43.06 cc. of a permanganate solution which has a $Na_2C_2O_4$ value of 6.70 mg. per cubic centimeter. Calculate the percentage of CaO in the mineral.

88. In the standardization of a dichromate solution, a sample of pure iron weighing 0.2000 g. is converted into 200 cc. of ferrous chloride solution, and titrated. In the subsequent analysis of an ore with the dichromate solution, an equal quantity of ferrous iron is present, but the solution to be titrated has a volume of 600 cc. If the indicator used permits the recognition of one part by weight of ferrous iron in 100,000 of solution, what error results from the fact that the two titrations are made at different volumes? (Assume that the dichromate solution was found to be 0.1000 N, and that the solutions have the specific gravity of water.)

89. A sample of crystalline ammonium acetate weighing 2.021 g. is dissolved in water and made up to 200.0 cc. One half of this solution is distilled with an excess of lime, and the distillate received in 25.00 cc. of 0.500 N acid; the second half is distilled with phosphoric acid in excess, and the distillate received in 45.00 cc. of 0.500 N alkali. In the first case, with methyl orange, the excess of acid requires 10.20 cc. of the standard alkali, and in the second case, with phenolphthalein, the excess of alkali requires 15.52 cc. of the standard acid. Calculate the formula of the salt.

90. The aqueous solution of 0.1361 g. of a mixture containing only sodium chloride and bromide is treated, in the presence of nitric acid, with 25.00 cc. of 0.1000 N $AgNO_3$ solution, and the precipitate is filtered off and washed. The filtrate and washings require 9.70 cc. of 0.1000 N thiocyanate solution. Calculate the percentages of sodium chloride and bromide in the sample.

91. A mixture containing soluble chlorides and iodides weighs 0.4500 g. This is treated, in the presence of nitric acid, with 35.00 cc. of 0.1000 N silver nitrate solution, and the precipitate is found to weigh 0.5000 g. The excess of silver nitrate in the filtrate and washings requires 11.10 cc. of

0.0500 N thiocyanate solution. Calculate the percentages of chlorine and iodine in the original mixture.

92. To 20.00 cc. of a solution of prussic acid, an excess of sodium hydroxide and a very little potassium iodide are added; this solution is titrated with 0.1000 N silver nitrate, of which 48.73 cc. are required to produce a faint permanent turbidity of silver iodide. Calculate the percentage of HCN in the original solution, assuming its specific gravity to be equal to that of water.

93. A mixture containing potassium cyanide and chloride, and weighing 0.2037 g., is dissolved in water and titrated with 0.1000 N silver nitrate solution, of which 14.41 cc. are required to produce a faint permanent turbidity. 16.19 cc. more of the silver nitrate solution are added, the solution is slightly acidified with nitric acid, and the filtrate and washings from the precipitate require for titration 14.51 cc. of 0.1000 N thiocyanate solution. Calculate the percentages of KCN and KCl in the sample.

94. A solution of potassium permanganate is equivalent to 5.00 mg. of iron per cubic centimeter. To 40.0 cc. of this solution, acidified with an excess of very dilute sulphuric acid, an excess of potassium iodide is added, and the liberated iodine is titrated with a solution of sodium thiosulphate, of which 34.85 cc. are required. Calculate the normality factor of the thiosulphate solution.

95. A sample of soda weighing 4.973 g. is dissolved in water and made up to one liter. A 100.0 cc. portion of this solution, carefully titrated in the cold with phenolphthalein as an indicator, requires 48.90 cc. of 0.0998 N acid. A second portion of 100.0 cc. is titrated with 0.499 N acid, of which 13.81 cc. are required with methyl orange as an indicator. Calculate the percentages of Na_2CO_3 and NaOH in the sample. (Cf. Problem 61.)

96. A sample of bleaching powder weighing 7.092 g. is triturated with water and made up to one liter. A 50.0 cc. portion of this suspension, when titrated with 0.1000 N arsenious acid, with potassium iodide-starch paper as an outside indicator, is found to require 26.15 cc. of the standard solution. What is the percentage of available chlorine in the bleaching powder?

97. If 43.60 cc. of a thiosulphate solution require 40.15 cc. of an iodine solution, and if 0.2118 g. of As_2O_3 require 42.40 cc. of the iodine solution, what is the normality factor of each solution?

98. A sample of titaniferous ore weighing 0.3805 g. is fused with a mixture of $K_2S_2O_7$ and KF, the melt dissolved in HCl, and the iron and titanium reduced with zinc in an atmosphere of hydrogen. The solution is then titrated in an atmosphere of carbon dioxide, in the presence of 1 g. of KSCN as the indicator, with 0.1000 N ferric chloride solution, of which 19.34 cc.

are required.   Calculate the percentage of TiO_2 in the ore.   ($TiCl_3 + FeCl_3$ $= TiCl_4 + FeCl_2$.)

99. In 50.0 cc. of a solution, containing both ferrous and ferric sulphates, the ferrous iron is titrated in the presence of sulphuric acid with 0.1000 N permanganate solution, after which the oxidized solution is titrated for total iron with 0.0997 N titanous chloride solution, with potassium thiocyanate as the indicator. If in the first titration 27.17 cc. of the permanganate solution are used, and in the second titration 46.98 cc. of the titanous chloride solution, what is the content of the original solution in grams per liter of ferrous and of ferric iron?

100. The ammonium phosphomolybdate precipitate obtained from 2.000 g. of steel is dissolved in dilute aqueous ammonia, the solution acidified with sulphuric acid, and the molybdenum reduced to the trivalent condition by passing the acid solution through a Jones' reductor, — the reduced solution being caused to enter the receiving vessel under the surface of a solution of ferric sulphate (2 $MoO_3 + 6$ $H = Mo_2O_3 + 3$ H_2O; and $Mo_2O_3 + 3$ $Fe_2O_3 = 2$ $MoO_3 + 6$ FeO). The resulting solution is at once titrated with a standard solution of permanganate, of which 18.75 cc. are required. If the permanganate solution has an iron value of 0.00540 g. per cubic centimeter, what is the percentage of phosphorus in the steel?

PART V

QUESTIONS

Exercises with the Balance.

1. What is the purpose of weighing?
2. Explain the mechanical theory of the balance.
3. Give five conditions which must be satisfied by a good balance.
4. What conditions must be fulfilled in order that a balance may be considered properly adjusted for use?
5. How may the zero-point of a balance be determined? Illustrate.
6. Explain the following methods of weighing: (a) Ordinary method; (b) Weighing by double vibrations; (c) Method of Gauss; (d) Method of Borda.
7. Describe a procedure for the calibration of a set of weights.
8. Discuss the errors in weighing which may be due: (a) to inequalities in length in the beam arms; (b) to the buoyancy of the atmosphere.
9. What is a desiccator? Explain why it is necessary, and give the principles upon which its use is based.

The Determination of Chlorine.

1. What substances would, if present, interfere with this determination?
2. Why should the solution be acidified with nitric acid? Why should a large excess of nitric acid be avoided?
3. Why should the solution not be heated until after the addition of the silver nitrate? Why is it then heated?
4. What are the advantages of washing by decantation? In washing a precipitate, whether by decantation or otherwise, why should the liquid each time be removed as far as possible before the addition of fresh wash liquid?
5. How can you tell when the precipitate has been sufficiently washed?
6. Why is the filter paper ignited separately from the bulk of the precipitate? What is the object of the treatment with nitric and with hydrochloric acid? Explain.
7. What is the effect of light upon silver chloride? Is the action of diffused daylight a serious source of error?

178

8. Why should the precipitate be heated until it just begins to fuse? What is the effect of overheating? Of underheating?

9. Water saturated with silver chloride at 100° contains about 22 mg. of the salt per liter. Explain why the precipitate may be thoroughly washed with hot water without undue loss. What is the solubility of silver chloride in water at the ordinary room temperature? In the precipitation of chloride ion, why should silver nitrate be added in moderate excess?

10. Given an aqueous solution of silver chloride in equilibrium with a quantity of the solid salt: What would happen upon the addition of (*a*) a few drops of silver nitrate solution? (*b*) a few drops of sodium chloride solution? (*c*) a large excess of sodium chloride? Explain in each case.

11. How may the crucible safely and readily be cleaned after the ignition of the silver chloride? Write equations to show the reactions involved.

12. (*a*) Explain the solubility of silver chloride in each of the following substances: aqueous ammonia; potassium cyanide solution; sodium thiosulphate solution. (*b*) Is silver iodide soluble in aqueous ammonia? In a solution of potassium cyanide? Explain your answers.

13. What other substances may be determined in a similar manner in the form of insoluble silver salts?

14. Why are Gooch crucibles preferable to ordinary paper filters; especially, for example, in the determination of iodides, cyanides, etc.?

15. Starting with the native mineral, describe the treatment which renders the asbestos suitable for use in the preparation of Gooch crucibles.

The Determination of Iron and of Sulphur in a Soluble Sulphate of Iron.

Iron. — 1. A mixture consists of ferric sulphate, sodium carbonate, and potassium sulphate, each of which is soluble in cold water. Will the mixture dissolve in water? Illustrate your answer by means of equations.

2. How is the sample taken into solution for this analysis?

3. In the precipitation with ammonium hydroxide, why must the iron be present wholly in the ferric condition?

4. How is the ferrous iron oxidized in this analysis? Write the equation. How can you tell when the oxidation is complete?

5. How may it be ascertained whether the original sample contains ferrous iron? Is it worth while to make this test? Why?

6. What advantage is to be gained by adding the ferric salt solution to an excess of aqueous ammonia, rather than the ammonia to the ferric salt solution? Explain.

7. How is the first precipitate of ferric hydroxide treated, and why? Explain in full.

8. Is it necessary to completely wash out the ammonium chloride before the ferric hydroxide is ignited? Why?

9. What precautions are to be observed in igniting the precipitate of ferric hydroxide?

10. Name two other metals which may be determined by a similar procedure. What additional precautions should be taken in their determination, and why?

11. In the determination of these three metals, would it be equally well to use sodium hydroxide as the precipitating reagent? Give the reason for your answer in the case of each metal.

12. What is the effect of tartaric or citric acid, sugars, etc. upon the precipitation of ferric hydroxide by means of ammonium or sodium hydroxide? Do any other metallic ions behave like Fe^{+++}-ion in this respect? Explain.

Sulphur. — 1. Why must nitrates be removed before the precipitation with barium chloride? How is this done? Write the reaction.

2. Name some other substances which, if present, should be removed before precipitation with barium chloride.

3. Why is barium chloride chosen as the reagent for sulphate, rather than lead nitrate or strontium chloride?

4. How many cubic centimeters of 1-normal barium chloride solution will be required to precipitate the sulphate from one gram of a sample containing 60% of $Fe_2(SO_4)_3$ and 14% of K_2SO_4?

5. What are the correct conditions for the precipitation of the sulphate? Explain in full.

6. What precautions should be observed in the ignition of the barium sulphate, and why?

7. What other substances may be determined as insoluble sulphates? What reagent is used in their precipitation?

The Determination of Sulphur in Ores.

1. Assuming complete oxidation, write an equation to show the action of nitric acid upon iron pyrites, FeS_2.

2. If pure FeS_2 were decomposed in this way with nitric acid, the iron precipitated with ammonia, and the filtrate evaporated with hydrochloric acid on the hot plate to dryness (to remove the nitrates), would there be any danger of losing a portion of the sulphur? Explain.

3. Explain the solubility of lead chloride in ammonium chloride solution. (Cf. the behavior of silver chloride.)

4. In the analysis of an ore containing lead, how may we prevent the precipitation of a portion of the sulphur as lead sulphate? Fully explain your answer.

5. Outline an experimental procedure for the determination of sulphur in heavy spar, $BaSO_4$.

The Determination of Phosphoric Anhydride in Phosphate Rock.

1. What are the chief components of phosphate rock? What other compounds are usually present? What is apatite?

2. Explain by means of the ionic theory and the solubility product law the fact that calcium phosphate, $Ca_3(PO_4)_2$, will dissolve in nitric acid.

3. Why is it necessary to remove any soluble silicic acid that may be present in the nitric acid solution of the mineral? How is this done?

4. Explain why it is possible, in washing the insoluble residue of silica, to make the test for calcium in the wash water by the addition of ammonia alone.

5. Why is it directed to neutralize the nitric acid solution with ammonia and then to make it slightly acid with nitric acid, before the addition of the molybdate reagent?

6. Why is an acid solution of ammonium nitrate used in washing the yellow precipitate? (Cf. question 9.) What would happen if this ammonium nitrate wash liquid were alkaline with ammonia? Explain.

7. Could the phosphorus be determined by igniting and weighing the yellow precipitate?

8. Why do we first precipitate the phosphate with molybdate solution instead of precipitating it directly from the original solution with magnesia mixture?

9. Explain why a large excess of the molybdate reagent is necessary for the complete precipitation of the phosphate.

10. Show by means of an equation the reaction between ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12 MoO_3$, and ammonium hydroxide. Sodium hydroxide.

11. What is magnesia mixture? What is the purpose of the ammonium chloride? Explain.

12. Why should the magnesium ammonium phosphate precipitation mixture be allowed to stand for some hours before filtering?

13. Why is dilute ammonia used in washing the precipitate of magnesium ammonium phosphate? Why not use water?

14. What precautions should be observed in the ignition of this precipitate, and why?

15. Name another element which may be determined by precipitation with magnesia mixture. Can any elements be determined in a similar manner by precipitation with sodium or ammonium phosphate? If so, name them.

16. If it were desired to determine the phosphorus in a sample of steel, in which it is present as iron phosphide, what would be the procedure? Explain.

The Analysis of Limestone.

1. What is the principal component of limestone? What other compounds are usually present? Why is it important to analyze a limestone?

2. What is the reason for the double evaporation with hydrochloric acid, followed by continued heating on the steam bath? When this residue is extracted with hydrochloric acid, what is the insoluble material that is left?

3. Why is the insoluble residue first washed with dilute acid rather than with water? Would cold water do about as well? Why?

4. What is the purpose of adding bromine water in the precipitation with ammonium hydroxide? Why must a large excess of ammonia be avoided?

5. Why should the ammonium hydroxide precipitate be filtered off promptly? Of what does this precipitate consist? How is this precipitate treated, and why?

6. How is the first ammonium oxalate precipitate treated, and why?

7. Explain why so little ammonium oxalate solution is added in the second precipitation of the calcium.

8. Explain the solubility of calcium oxalate in hydrochloric acid and its insolubility in acetic acid.

9. What reactions take place when calcium oxalate, $CaC_2O_4 . H_2O$, is ignited?

10. Why should the solution be only faintly ammoniacal for the precipitation of the magnesium? Why is more ammonia later added to the precipitation mixture? Why is the precipitation mixture then allowed to stand for several hours before filtration?

11. How is the first precipitate of magnesium ammonium phosphate treated? Explain why this is necessary. Is it possible to accomplish the same result in any other way, and if so how?

12. Why is the precipitate washed with dilute ammonia rather than with water?

13. Write an equation to show what happens when $MgNH_4PO_4 . 6 H_2O$ is ignited; when $Mg[(NH_4)_2PO_4]_2 . n H_2O$ is ignited.

14. What precautions should be observed in igniting the precipitate, and why?

15. Explain briefly the method described in the procedure for the determination of carbon dioxide.

16. What are the objections to this method? Under what conditions can the method be relied upon to furnish accurate results?

17. What modifications should be made in the procedure if the sample to be analyzed is a baking powder?

18. Explain the operation of the aspirator. Why is the carbon dioxide more readily removed when air is bubbled through the solution? (Cf. Part I, The Evaporation of Liquids.)

19. What method for the determination of carbon dioxide may be regarded as the converse of the method described in the procedure? Describe it.

20. Can you think of any other method for the exact determination of carbon dioxide?

The Determination of Silica in a Refractory Silicate.

1. Why is it essential to grind the whole of the sample very fine?

2. Write an equation to show the reaction between orthoclase, $KAlSi_3O_8$, and sodium carbonate, above the melting point of the latter. Why is a very large excess of the latter used?

3. How can you tell whether the decomposition is complete (a) by inspecting the mixture during fusion; (b) after the treatment of the melt with dilute acid?

4. Why is the fused mass treated with a considerable volume of dilute acid, rather than with concentrated acid?

5. How is the silica separated from the residue left upon evaporation with dilute hydrochloric acid? Explain.

6. What is the purpose of treating the silica with hydrofluoric and sulphuric acids? Explain in full.

7. How would you determine the percentage of mixed iron and aluminum oxides in an insoluble silicate? How would you determine the calcium oxide? The magnesium oxide?

8. How would you determine the silica in a silicate mineral which may be readily decomposed by hydrochloric acid?

The Determination of Potash.

1. Is this a precipitation method? If not, to what class does it belong?

2. Why is it necessary to remove hydrochloric and sulphuric acids before the extraction of the soluble perchlorates? How are these acids removed? Explain.

3. What weight of $HClO_4$ will be required to convert one gram of NaCl into $NaClO_4$? One gram of KCl into $KClO_4$? What connection exists between these questions and the procedure? (Cf. Part IV., Problem 30.)

4. Explain the fact that phosphates, even if insoluble in alcohol, need not be removed before making the extraction. What precaution should be observed when phosphates are present, and why?

5. Do any of the following salts interfere with the method; and, if so, how is the difficulty overcome? NH_4ClO_4, $Ba(ClO_4)_2$, $Mg(ClO_4)_2$.

6. Why is a small quantity of $HClO_4$ added to the alcohol to be used in the extraction? If 50 cc. of this liquid, capable of dissolving 2 mg. of pure $KClO_4$, are used in the extraction, why is not the quantity of $KClO_4$ found in the residue 2 mg. less than the true value?

7. How may we determine the point at which the extraction is complete? Explain.

The Electrolytic Determination of Copper.

1. Define: ampere; volt; ohm. State Ohm's law. State Faraday's laws.

2. Show by means of a diagram how the apparatus is assembled for an electrolytic determination.

3. Explain the electrolytic reduction of nitric acid to ammonia.

4. Explain the deposition of lead peroxide upon the anode, in the electrolysis of a solution containing lead nitrate and nitric acid.

5. What is meant by the discharge potential of an ion? The decomposition voltage of a salt? What is polarization? Explain in each case.

6. Explain why it is possible to separate copper from nickel by electrolysis? Can nickel be separated from cobalt in this way? Why?

7. What are the advantages of mechanical stirring during electrolysis?

8. What is meant by current density? What is the unit of current density? Why is current density a factor of the greatest importance in electro-analysis?

9. What factors favor the formation of a satisfactory deposit? What factors interfere with it?

10. Outline a method for the preparation of a solution suitable for electrolysis when the sample to be analyzed is a copper ore containing arsenic. Why should the arsenic be removed?

11. Discuss the materials from which electrodes may be prepared, and the form of the electrodes and electrolytic vessels.

12. Name the factors in the electrolytic work which should receive especial attention in an endeavor to make accurate and reliable copper determinations as rapidly as possible. Explain in the case of each factor mentioned.

Volumetric Analysis: Fundamental Principles.

1. Specify the chief uses of measuring flasks; of transfer pipettes; of burettes.

2. Describe the preparation of sulphuric acid-dichromate cleaning solution. How is it used?

3. In a titration with a solution correctly made up to tenth-normal concentration at 20°, a burette correctly graduated for use at 20° is used at an

actual temperature of 27.5°, and the indicated volume of solution withdrawn is 27.68 cc.; to how many cubic centimeters of tenth-normal solution does this liquid correspond? (See Part I.)

4. Define the term "liter."

5. Describe a method for the calibration of a 100-cc. measuring flask. Illustrate your description. (See Part I.)

6. What is a standard solution? A normal solution? Define and illustrate the term "normality factor."

7. Characterize in general the reactions which are suitable as the basis for volumetric processes.

8. What is an indicator? Illustrate your answer.

9. Discuss the advantages of the volumetric system.

Neutralization Methods: The Standardization of Acids and Alkalies.

1. Define in terms of the theory of ionization: (*a*) a neutral solution; (*b*) an acid solution; (*c*) an alkaline solution.

2. Will the solution resulting from mixing equal volumes of one-tenth normal aqueous solutions of the following substances be acid, alkaline, or neutral: (*a*) hydrogen chloride and sodium hydroxide; (*b*) hydrogen chloride and ammonium hydroxide; (*c*) acetic acid and sodium hydroxide?

3. Give a full explanation of case (*c*) above, writing all equations and equilibria.

4. What indicator should be used in each case in titrations involving the combinations indicated in question 2? Explain fully. (See the section on Indicators for Use in Alkalimetry and Acidimetry.)

5. Outline procedures for the preparation of approximately half-normal solutions of hydrochloric acid and sodium hydroxide.

6. Describe a method for obtaining the ratio between the solutions referred to in the preceding question. If 20.00 cc. of an acid solution require 21.46 cc. of 0.4693-normal alkali for neutralization, what is the normality factor of the acid?

7. Describe the sodium carbonate method for the standardization of a solution of hydrochloric acid. If 0.5383 g. of Na_2CO_3 require 20.15 cc. of the acid for neutralization, what is the normality factor of the acid?

8. If 10.00 cc. of a solution of hydrogen chloride yield 0.7421 g. of silver chloride, what is the normality factor of the acid?

9. Describe the standardization of sodium hydroxide solution by means of potassium bitartrate. If 1.179 g. of the latter require 13.35 cc. of the alkali for neutralization, what is the normality factor of the solution?

10. If 20.00 cc. of an acid are equivalent to 21.20 cc. of an alkali, and if 40.00 cc. of the acid are added to 0.6000 g. of Na_2CO_3 and the resulting solu-

tion requires 3.00 cc. of the alkali for neutralization, what are the normality factors of the two solutions?

11. Describe a method for the preparation of a solution of hydrochloric acid of exactly one-half normal concentration.

The Total Alkalinity of Soda Ash.

1. Discuss the composition of soda ash, and account for the impurities it is likely to contain.

2. Which of the impurities will contribute to the total alkaline strength of the soda ash?

3. Could this determination be made with phenolphthalein as the indicator, and if so how?

4. Give two volumetric methods for the determination of Na_2CO_3 and of NaOH in mixtures of the two substances.

5. Give a method for the determination of Na_2CO_3 and of $NaHCO_3$ in mixtures of the two salts.

The Neutralization Value of an Acid.

1. In titrating weak acids, why is it usually necessary to work at the boiling temperature?

2. At what point does an ice-cold, dilute solution of sodium hydroxide containing phenolphthalein lose its red color upon being treated with carbon dioxide? Upon boiling this decolorized solution, the color reappears; explain fully the mechanism by which the alkalinity of the solution increases on boiling.

3. Describe a method for the preparation of a carbonate-free solution of sodium hydroxide. How should such a solution be preserved? Why is its preparation sometimes worth while?

4. Is it possible to accurately titrate sulphurous acid with a standard solution of ammonia? If not, why? And if so, what indicator should be used?

The Determination of Protein Nitrogen by the Kjeldahl Method.

1. What is the purpose in the digestion of (*a*) the concentrated sulphuric acid? (*b*) The copper sulphate? (*c*) The potassium sulphate?

2. What chemical change does sulphuric acid undergo during the digestion? The organic matter?

3. Why is a long-necked flask used?

4. How would the procedure of digestion be modified if nitrates were present? Explain fully.

5. How would the procedure be modified if mercury were added instead of copper sulphate? Explain in full.

6. In what form does the nitrogen exist after the completion of the digestion? After making the solution alkaline with sodium hydroxide? In what form does it distill over?

7. How is the loss of ammonia prevented upon the addition of an excess of sodium hydroxide?

8. What is the purpose of the zinc? What is the action of sodium hydroxide solution upon zinc?

9. The ammonia from one gram of a fertilizer is distilled into 20.00 cc. of 0.5000 N acid, and 6.00 cc. of 0.4800 N alkali are required to neutralize the excess of acid; calculate the percentage of nitrogen in the sample.

10. If 0.20 cc. of 25.00% NaOH (sp. gr., 1.25) had been carried over by bumping or foaming, what ould have been the apparent percentage of nitrogen in the above case?

11. If you had to determine the percentage of NH_3 and of $HC_2H_3O_2$ in crude ammonium acetate, how would you proceed?

Dichromate Methods: The Titration of Iron.

1. Write the equation for the oxidation of ferrous chloride with potassium dichromate in the presence of hydrochloric acid.

2. What weight of $K_2Cr_2O_7$ is required for one liter of a tenth-normal solution, to be used as an oxidizing agent?

3. Outline the procedure for the standardization of dichromate solution by means of iron wire. Why is it well also to have a standard solution of ferrous ammonium sulphate, and how is this solution standardized?

4. What is the maximum weight of pure iron wire which can be taken for reaction with tenth-normal dichromate without having to refill a 30-cc. burette?

5. Name four reagents which can be used to reduce ferric salts to ferrous, in the presence of hydrochloric acid, and write the equation in each case.

6. Why is it necessary after reduction with stannous chloride to add mercuric chloride to the solution? Why must the stannous chloride be present only in very slight excess (equations)? Why should hydrochloric acid be present during the titration?

7. What indicator is used in the titration? What action has it upon ferric salts? Upon ferrous salts?

8. Why is the indicator used outside of the solution?

9. What products are formed when chromite, $Fe(CrO_2)_2$, is fused with sodium peroxide? What happens upon treating the fused mass with water? Why is the aqueous solution boiled? What then happens when the filtrate is acidified with sulphuric acid? How may the chromium in the resulting solution be determined volumetrically?

Permanganate Methods: The Titration of Iron and of Oxalic Acid.

1. How many grams of $KMnO_4$ are required for one liter of tenth-normal solution, to be used as an oxidizing agent in acid solutions? To be used in neutral solutions for the oxidation of manganese?

2. Why should a permanganate solution be allowed to stand for several days, and then be filtered through asbestos, before it is standardized? Why should it not be placed in burettes having rubber outlet tubes?

3. Name at least four substances which can be used to standardize permanganate solutions. Write an equation in each case.

4. What is the maximum weight of $Na_2C_2O_4$ which can be titrated with tenth-normal permanganate solution without having to refill a 30-cc. burette?

5. In the titration of oxalic acid, why is it that the oxidation proceeds so much more slowly at first than later on? Explain in full.

6. Name ten substances which can be quantitatively determined by means of potassium permanganate.

7. What effect does potassium permanganate have upon hydrochloric acid in the presence of ferrous salts, even in very dilute solution? How may this action be prevented?

8. What are the components of the Zimmermann-Reinhardt solution? Explain the purpose of each.

9. Under what conditions can ferrous iron be accurately determined with potassium permanganate without the use of the Zimmermann-Reinhardt solution?

10. What is the maximum weight of a sample of ore containing 40.00% of iron which can be taken for titration with tenth-normal oxidizing agent without having to refill a 30-cc. burette?

11. Discuss the preparation of a solution for analysis from a refractory iron ore.

12. Describe a method for the determination of calcium by means of potassium permanganate.

13. Outline a method for the determination of the oxidizing power of pyrolusite by means of oxalic acid and potassium permanganate.

14. How can the determination referred to in the preceding question be made by a gravimetric process?

The Determination of Phosphorus in Steel.

1. Assuming the presence of the phosphorus as Fe_3P_2, show by means of an equation the action of nitric acid upon this compound. Why is the nitric acid solution heated with potassium permanganate?

2. In order to cause the higher oxides of manganese, such as MnO_2, to

go into solution in nitric acid, what kind of a reagent should be added? Illustrate and explain.

3. What is the purpose of precipitating the phosphorus as ammonium phosphomolybdate?

4. Why is the yellow precipitate dissolved in ammonia and the solution acidified with sulphuric acid, rather than to dissolve it directly in sulphuric acid? Why is MoO_3 not precipitated when the ammoniacal solution is acidified with sulphuric acid? Would hydrochloric or nitric acid do as well here, and why?

5. Describe the construction and use of the Jones reductor. Can it be used for the reduction of substances other than molybdenum?

6. Why is it best to receive the reduced molybdenum solution below the surface of a solution containing ferric alum? What is the purpose of the phosphoric acid in this solution?

7. How should the permanganate solution be standardized in order to obtain the most reliable results?

8. Would you recommend the determination of phosphoric anhydride in apatite by this method? Why? Is there a suitable volumetric method? If so, describe it.

The Determination of Manganese in an Ore.

1. What is the Guyard reaction? What rôle does it play in the titration of oxalic acid or of iron with potassium permanganate?

2. Discuss the preparation of the solution for analysis from a refractory ore containing manganese.

3. What happens when zinc oxide is added to the acid solution of the ore (equations)?

4. Explain fully why a zinc salt should be present in the solution during the titration.

5. Explain why the presence of chlorides does not interfere with the accuracy of this titration.

6. If the permanganate solution used in this titration is $0.1000\text{-}N$ for use with iron or oxalic acid, what is its normality factor for this reaction?

7. How is it best to standardize the permanganate solution used in this determination?

Iodometric Methods: The Preparation and Standardization of Iodine and Thiosulphate Solutions.

1. How many grams of iodine are required for one liter of the tenth-normal solution? Of sodium thiosulphate, $Na_2S_2O_3 . 5 H_2O$?

2. How is the iodine solution made, and what is the purpose of the potassium iodide? Show what equilibria exist in the iodine solution. Why

should the water be freshly boiled and allowed to cool out of contact with the air, in the preparation of the thiosulphate solution?

3. Write the reaction between iodine and sodium thiosulphate. How do chlorine and bromine differ from iodine in their behavior towards sodium thiosulphate? Explain why this is so.

4. What is the effect of free carbonic acid upon sodium thiosulphate solution? Does the decomposition cease as soon as all of the carbonic acid has reacted? Write equations to illustrate your answers.

5. Does the solution resulting from the partial decomposition of the thiosulphate have a greater or lower reducing value than the original solution? Explain why.

6. Give equations to show two ways in which iodine may act as an oxidizing agent.

7. What is the maximum weight of As_2O_3 which can be taken for reaction with tenth-normal iodine solution without having to refill a 30-cc. burette?

8. Can the standardization of iodine against arsenious oxide be performed in a strongly alkaline solution? Can it be done in an acid solution? Give reasons for your answers.

9. What is the purpose of the sodium bicarbonate? Is the bicarbonate solution acid, alkaline, or neutral? Explain your answer.

10. Discuss the determination of the end-point. Explain why the indicator is added in such large quantity.

11. Discuss the use of iodine solutions in the presence of sulphuric acid. In the presence of ammonium salts.

The Determination of Antimony in Stibnite.

1. Write the reaction between pure stibnite and hydrochloric acid.

2. Why must the hydrochloric acid solution be heated on the steam bath? Why must it not be boiled until after dilution?

3. What is the purpose of adding tartaric acid to the solution? Explain.

4. Explain why the solution may possibly turn red during gradual dilution. What is the correct procedure in such a case?

5. If a white precipitate forms upon dilution, what error has been made? What is the white precipitate, and what should be done with the mixture?

6. What is the purpose of almost neutralizing the solution with sodium hydroxide, and how is this accomplished? Why is sodium bicarbonate then added in large excess?

7. What elements would, if present, interfere with this determination, and why?

The Determination of Lead in an Ore.

1. After the decomposition of the ore and the addition of sulphuric acid, why is it necessary to evaporate to white fumes?

2. Explain the solubility of lead sulphate in ammonium acetate solution.

3. Explain why it is possible to quantitatively precipitate the lead from the ammonium acetate solution by means of an excess of potassium dichromate.

4. Explain the solubility of lead chromate in the acidified solution of sodium chloride.

5. Write an equation to show the reaction of the acid chromate solution with potassium iodide.

6. Why should the thiosulphate solution used in this determination be standardized under identical conditions against test lead?

The Determination of Copper in an Ore.

1. In this determination, why is the copper separated from the other metals present in the ore? Explain how iron, arsenic, or antimony would interfere with the accuracy of the titration.

2. What would you expect the composition of the precipitate to be which is formed upon the addition of sodium thiosulphate to a solution of copper sulphate? How does it happen, then, that we obtain cuprous sulphide?

3. Can any other metals be precipitated from their salt solutions by means of sodium thiosulphate? (Try, for example, silver nitrate and sodium thiosulphate, in the cold, and explain what takes place.)

4. What is the object of igniting the precipitate of cuprous sulphide? What becomes of any antimony which is present?

5. Why is it so important to standardize the thiosulphate solution against pure metallic copper?

6. Why must the nitrous fumes be completely expelled before the addition of the potassium iodide?

7. Why is it preferable to titrate the free iodine in the presence of acetic acid, rather than in the presence of sulphuric acid? Explain fully.

8. Write an equation to show the action of nitric acid upon cuprous iodide.

Precipitation Methods: The Determination of Chlorine.

1. Briefly outline the procedure for the standardization of the silver nitrate and potassium thiocyanate solutions against pure sodium chloride. Could these solutions be standardized against pure metallic silver, and if so how?

2. How may pure sodium chloride be prepared from the commercial salt?

3. What indicator is used in connection with thiocyanate solutions? Why must nitric acid be present? Explain fully why the indicator should be added in such large quantity.

4. At 18–20°, the solubility product of silver chloride is about 0.6×10^{-10} and that of silver thiocyanate is about 0.6×10^{-12}; what is the relative concentration of the chloride and thiocyanate ions in a solution which is saturated with both salts? Assume the equal (practically complete) ionization of both salts.

5. Why is it necessary to filter off the silver chloride before making the titration with the thiocyanate solution? Base your explanation upon the data given in the preceding question.

6. In general, what anions may be determined by this method without first filtering off the silver salt?

7. How may the halogens in alkali chlorates, bromates, and iodates be determined by this method?

8. Outline a procedure for the determination by this method of (*a*) the chlorine in horn silver, AgCl; (*b*) the silver in the same mineral.

APPENDIX

THE PREPARATION OF THE REAGENTS

Many of the reagents used in quantitative analysis are prepared for one specific purpose only, and directions for the preparation of such reagents will be found in the treatment of the individual determinations. Certain reagents, however, are used at approximately fixed concentrations in a variety of processes, and it is especially these which are included in this section.

There are many advantages in making the concentrations of the reagents used in analytical work follow a definite system. The most convenient system is to use multiples or submultiples of the equivalent weight employed in volumetric analysis, though of course the concentration of the solution need not be known with such exactitude as in volumetric work.

With this system, equal volumes of the solutions bear fixed relations to one another, it is easy to calculate the volume of a reagent which is required for a specific purpose, and the addition of an unnecessary excess may readily be avoided. This means a saving in time, labor, and material; and it leads to more accurate and reliable work. Thus, if it is directed to fuse one gram of a silicate, say $KAlSi_3O_8$, with 7.5 g. of Na_2CO_3 and to take up the cooled mass with water and an excess of hydrochloric acid, we know that 24 cc. of 6-normal acid will suffice to neutralize the mixture (since 7.5 g. of Na_2CO_3 correspond to about one seventh of an equivalent of this salt), and that 30 cc. in all will furnish a sufficient excess. If the mixture is evaporated to dryness in the regular manner and taken up with 2 cc. of 12-normal hydrochloric acid and a little water, it

o   193

will be obvious that 4 cc. of 6-normal ammonium hydroxide will suffice to neutralize the acid; and that 8 cc. in all will neutralize the acid, precipitate the aluminum, and in addition furnish a sufficient excess.

Measuring cylinders and measuring pipettes are useful for delivering specific volumes of such reagents.

ACIDS

Acetic, 6-normal: Mix 350 cc. of glacial acetic acid with 650 cc. of water.

Hydrochloric, 12-normal: Use the C. P. acid of commerce of sp. gr., 1.19.

Hydrochloric, 6-normal: Mix 12-normal acid with an equal volume of water. The specific gravity of this acid is about 1.10.

Nitric, 16-normal: Use the C. P. acid of commerce of sp. gr., 1.42.

Nitric, 6-normal: Mix 380 cc. of the 16-normal acid with 650 cc. of water. The specific gravity of this acid is about 1.195.

Sulphuric, 36-normal: Use the C. P. acid of commerce of sp. gr., 1.84.

Sulphuric, 6-normal: Pour 200 cc. of the 36-normal acid into 1045 cc. of water. The specific gravity of this acid is 1.18.

BASES

Ammonium hydroxide, 15-normal: Use the C. P. ammonia water of commerce of sp. gr., 0.90.

Ammonium hydroxide, 6-normal: Mix 400 cc. of the 15-normal solution with 600 cc. of water. The specific gravity of this solution is about 0.958.

Sodium hydroxide, 6-normal: Dissolve 250 g. of stick sodium hydroxide in water and dilute to one liter.

SALTS

Ammonium carbonate: Dissolve 250 g. of freshly powdered ammonium carbonate in one liter of 6-normal ammonium hydroxide, and filter if there is a residue.

Ammonium molybdate:[1] Dissolve 100 g. of MoO_3 in 80 cc. of ammonia (sp. gr., 0.90) with the addition of 400 cc. of water; with cooling and constant stirring, allow the clear solution to run slowly into a mixture of 400 cc. of nitric acid (sp. gr., 1.42) with 600 cc. of water, add 0.05 g. of microcosmic salt, $NaNH_4HPO_4 . 4 H_2O$, and keep the mixture in a warm place for several days, or until a portion heated to 40° deposits no yellow precipitate. Decant from any sediment, and preserve in glass-stoppered bottles. This solution contains 68 g. of MoO_3 per liter.

Ammonium oxalate, 0.5-normal: Dissolve 35.5 g. of $(NH_4)_2C_2O_4 . H_2O$ in 1000 cc. of water.

Barium chloride, 1-normal: Dissolve 122 g. of $BaCl_2 . 2 H_2O$ in 1000 cc. of water.

Magnesia mixture, 0.5-normal as a precipitant for phosphoric or arsenic acid: Dissolve 51 g. of $MgCl_2 . 6 H_2O$ and 130 g. of NH_4Cl in water, add 121 cc. of ammonia (sp. gr., 0.90), and dilute to one liter.

Mercuric chloride, 0.2-normal for oxidizing stannous chloride: Dissolve 54 g. of $HgCl_2$ in 1000 cc. of hot water.

Silver nitrate, 0.2-normal: Dissolve 34 g. of $AgNO_3$ in 1000 cc. of water.

Sodium phosphate, 0.5-normal as a precipitant for magnesium: Dissolve 90 g. of $Na_2HPO_4 . 12 H_2O$ (or 52 g. of $NaNH_4HPO_4 . 4 H_2O$) in 1000 cc. of water.

Stannous chloride, 1-normal as a reducing agent: Dissolve 113 g. of $SnCl_2 . 2 H_2O$ in 150 cc. of 12-normal hydrochloric acid, with the gradual addition of water, finally diluting to one liter. Keep in bottles containing granulated tin.

[1] *Recovery of the Molybdic Acid.* To the liquid molybdate residues, acidified if necessary with nitric acid, add sodium phosphate solution in excess. Collect the yellow precipitate, wash it with water containing sodium sulphate, and then dry it in the air. Dissolve 1 Kg. of the dried precipitate in ammonia, add a strong solution of 60 g. of NH_4Cl and 120 g. of $MgCl_2 . 6 H_2O$ in water, allow to stand for 6 hours, and filter off the precipitate. To the filtrate, decolorized if necessary with a little H_2O_2, add HCl just to acid reaction, to precipitate the MoO_3. Collect this precipitate, wash with water, and dry at 110°.

Sulphuric Acid–Dichromate Cleaning Solution

With stirring, cautiously pour 200 cc. of sulphuric acid (sp. gr., 1.84) into 150 cc. of cold water, and saturate the hot solution, without further heating, with powdered sodium (or potassium) dichromate.

When cleaning measuring vessels with this liquid, they should be filled with the *cold* solution and allowed to stand overnight, or longer.

Analytical Samples for the Use of Students

The analyzed samples indicated in the text for the use of beginners in quantitative analysis may in some cases be obtained in the market. Otherwise, they may be prepared by mixing together the component materials in the proportions decided upon. This mixing is best accomplished by long continued grinding in a ball mill, the material being finally passed through a fine-meshed sieve, and bottled. These samples should be carefully analyzed by members of the quantitative staff, so that the student's work may be judged according to its accuracy. Most of the mixtures indicated can be kept from year to year without change.

It is desirable to have in each case a continuous series of at least ten samples, varying in content from sample to sample by about 0.4–0.5%.

APPARATUS IN THE STUDENT'S DESK [1]

QUANTITATIVE CHEMICAL LABORATORIES

Above in the drawers

1 Brush, camel's hair.
1 Burette, g. s., 30 cc.
1 Burette, 30 cc., for pinchcock.
4 Crucibles, porcelain, o.
2 Crucibles, porcelain, Gooch, extra disc.
2 Cylinders, graduated, 50 cc. and 10 cc.
1 File.
1 Forceps, steel.
2 Funnels, diam. 25 mm., stem 40 mm.
2 Glasses, watch, 140 mm.
2 Glasses, watch, 70 mm.
2 Glasses, watch, 50 mm.
1 Vial litmus paper, blue.
1 Vial litmus paper, red.
2 Boxes matches, safety.
1 Pinchcock.
1 Pipette, 25 cc.
1 Pipette, 10 cc.
2 Policemen, rubber tip.
3 Rods, glass, 200 mm.
6 Test tubes.
1 Thermometer, 100° C.
1 Tongs, brass, nickel plated.
1 Tube, connecting, 3-way.
2 Tubes, rubber, for Gooch crucibles.
3 Tubes, weighing, with corks.
1 Tube, rubber, pressure, length 300 mm.
1 Tube, rubber, small, length 300 mm.
Tubing, soft glass, 900 mm.

Below in the cupboard

12 Beakers, 2 nests, 1–6, with window pane.
2 Bottles, g. s., 2500 cc.
1 Bottle, g. s., 250 cc., for cleaning solution.
1 Bottle, g. s., 125 cc., for silver nitrate.
1 Bottle, weighing.
1 Burette holder, Lincoln's.
2 Burners, adjustable.
2 Burner tubes, rubber.
2 Casseroles, porcelain, 500 cc.
1 Desiccator for 4 crucibles.
2 Flasks, Erlenmeyer, 500 cc.
2 Flasks, Erlenmeyer, 250 cc.
2 Flasks, Erlenmeyer, 150 cc.
2 Flasks, filter, 500 cc.
2 Flasks, Florence, 500 cc.
2 Flasks, Florence, 250 cc.
2 Flasks, Florence, 50 cc., for indicators.
1 Flask, volumetric, 1000 cc.
1 Flask, volumetric, 500 cc.
2 Flasks, volumetric, 250 cc.
4 Funnels, diam. 70 mm., stem 200 mm.
2 Funnels, for Gooch crucibles.
1 Sponge.
1 Stand, filter, wooden.
2 Stands, iron, 1 ring each.
2 Triangles, pipe stem, new form.
2 Tripods, iron.
2 Wire gauzes.

[1] The articles listed above represent the apparatus with which it is desirable to provide each student at the outset; the list can of course be modified in many particulars without jeopardizing the success of the work. Any additional apparatus which may be required can be obtained as needed from the store room.

N	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4 8 12	17 21 25	29 33 37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4 8 11	15 19 23	26 30 34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3 7 10	14 17 21	24 28 31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3 6 10	13 16 19	23 26 29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3 6 9	12 15 18	21 24 27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3 6 8	11 14 17	20 22 25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3 5 8	11 13 16	18 21 24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2 5 7	10 12 15	17 20 22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7	9 12 14	16 19 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7	9 11 13	16 18 20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 16 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 4 5	7 9 10	12 14 16
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 12 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	5 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 7 8	9 11 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 2 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 4	5 6 7	8 9 11
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 6	7 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 5 6	7 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 3	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
N	0	1	2	3	4	5	6	7	8	9	1 2 2	4 5 6	7 8 9

The proportional parts are stated in full for every tenth at the right-hand side. The logarithm of any number of four significant figures can be read directly by add-

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	1	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	3	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	3	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	3	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	3	3	4	4	5	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	3	3	4	4	5	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	4	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	1	1	2	2	3	3	4	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ing the proportional part corresponding to the fourth figure to the tabular number corresponding to the first three figures. There may be an error of 1 in the last place.

	0	1	2	8	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0 0 1	1 1 1	2 2 2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0 0 1	1 1 1	2 2 2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0 0 1	1 1 1	2 2 2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0 0 1	1 1 1	2 2 2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0 1 1	1 1 2	2 2 2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0 1 1	1 1 2	2 2 2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0 1 1	1 1 2	2 2 2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0 1 1	1 1 2	2 2 2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0 1 1	1 1 2	2 2 3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0 1 1	1 1 2	2 2 3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0 1 1	1 1 2	2 2 3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0 1 1	1 2 2	2 2 3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0 1 1	1 2 2	2 2 3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0 1 1	1 2 2	2 3 3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0 1 1	1 2 2	2 3 3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0 1 1	1 2 2	2 3 3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0 1 1	1 2 2	2 3 3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0 1 1	1 2 2	2 3 3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0 1 1	1 2 2	2 3 3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0 1 1	1 2 2	2 3 3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0 1 1	1 2 2	3 3 3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0 1 1	1 2 2	3 3 3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0 1 1	2 2 2	3 3 3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0 1 1	2 2 2	3 3 3
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0 1 1	2 2 2	3 3 4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0 1 1	2 2 3	3 3 4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0 1 1	2 2 3	3 3 4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0 1 1	2 2 3	3 3 4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0 1 1	2 2 3	3 4 4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0 1 1	2 2 3	3 4 4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0 1 1	2 2 3	3 4 4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0 1 1	2 2 3	3 4 4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0 1 1	2 2 3	3 4 4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0 1 1	2 2 3	3 4 4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1 1 2	2 3 3	4 4 5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 3	4 4 5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 3	4 5 5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1 1 2	2 3 3	4 5 5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1 1 2	2 3 4	4 5 5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1 1 2	2 3 4	4 5 6
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1 1 2	2 3 4	4 5 6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1 1 2	2 3 4	4 5 6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1 1 2	3 3 4	4 5 6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1 1 2	3 3 4	5 5 6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1 1 2	3 3 4	5 5 6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1 1 2	3 3 4	5 6 6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1 1 2	3 3 4	5 6 6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1 1 2	3 4 4	5 6 6

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1 1 2	3 4 4	5 6 7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1 1 2	3 4 4	5 6 7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1 1 2	3 4 5	5 6 7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1 2 2	3 4 5	6 6 7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1 2 2	3 4 5	6 6 7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1 2 2	3 4 5	6 7 7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1 2 2	3 4 5	6 7 8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1 2 3	3 4 5	6 7 8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1 2 3	3 4 5	6 7 8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1 2 3	4 5 5	6 7 8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1 2 3	4 5 6	7 8 8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1 2 3	4 5 6	7 8 9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1 2 3	4 5 6	7 8 9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1 2 3	4 5 6	7 8 9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1 2 3	4 5 6	7 8 9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1 2 3	4 5 6	7 8 9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1 2 3	4 5 6	7 9 10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1 2 3	4 5 7	8 9 10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1 2 3	5 6 7	8 9 10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1 2 3	5 6 7	8 9 10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1 2 3	5 6 7	8 9 10
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1 2 4	5 6 7	8 10 11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1 2 4	5 6 7	9 10 11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1 3 4	5 6 7	9 10 11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1 3 4	5 6 8	9 10 12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1 3 4	5 7 8	9 11 12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1 3 4	5 7 8	9 11 12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1 3 4	5 7 8	10 11 12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1 3 4	6 7 8	10 11 13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1 3 4	6 7 9	10 11 13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1 3 4	6 7 9	10 12 13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2 3 5	6 8 9	11 12 14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2 3 5	6 8 9	11 12 14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2 3 5	6 8 9	11 13 14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2 3 5	6 8 9	11 13 15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2 3 5	7 8 10	12 13 15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2 3 5	7 8 10	12 14 15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2 4 5	7 9 10	12 14 16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2 4 5	7 9 11	12 14 16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2 4 6	7 9 11	13 15 16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2 4 6	7 9 11	13 15 17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2 4 6	8 9 11	13 15 17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2 4 6	8 10 12	14 15 17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2 4 6	8 10 12	14 16 18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2 4 6	8 10 12	14 16 18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2 4 6	8 10 12	15 17 19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2 4 6	9 11 13	15 17 19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2 4 6	9 11 13	15 17 19
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2 4 7	9 11 13	16 18 20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2 5 7	9 11 14	16 18 21

INDEX

UNIVERSITY OF CALIFORNIA
DEPARTMENT OF CIVIL ENGINEERING
BERKELEY. CALIFORNIA

INTERNATIONAL ATOMIC WEIGHTS, 1917

Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	191.9
Bromine	Br	79.92	Oxygen	O	16.000
Cadmium	Cd	112.40	Palladium	Pd	106.7
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	173.5
Lutetium	Lu	175.0	Yttrium	Yt	88.7
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			